

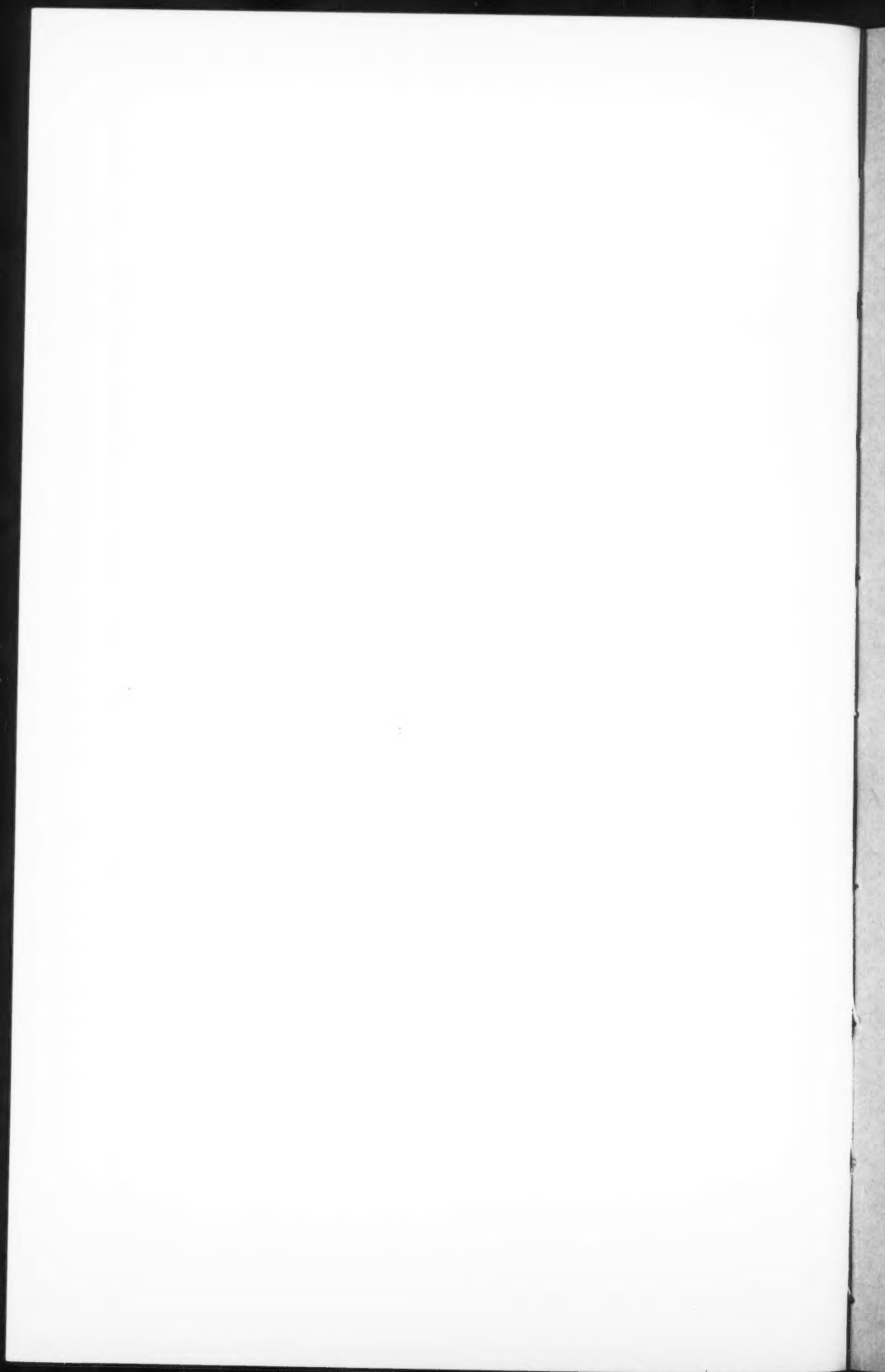
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***Editor:* G. A. LEDINGHAM**

***Published by* THE NATIONAL RESEARCH COUNCIL  
OTTAWA CANADA**



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*Editor:* G. A. LEDINGHAM

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OTTAWA CANADA

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## AN APPARATUS FOR DIFFERENTIAL THERMAL ANALYSIS<sup>1</sup>

BY J. G. BRADY,<sup>2</sup> R. L. EAGER,<sup>3</sup> AND J. M. HUMPHRYS<sup>4</sup>

### ABSTRACT

An apparatus which has been used to determine the mineralogical composition of some Saskatchewan clays and volcanic ashes by differential thermal analysis is described. A furnace of the horizontal muffle type was used to raise the temperature of the sample and of the inert material. Several types of containers for the sample and for the inert material were tried. In the final design the containers were constructed from 0.002 in. thick platinum foil as it was found that the best results were obtained if the containers had low heat capacities. A 28 gauge chromel-alumel differential thermocouple was used. The furnace temperature and the differential temperature were both recorded on a two-point strip chart recorder. Satisfactory results, a few of which are described in the present paper, were obtained with this apparatus.

### INTRODUCTION

During heating or cooling a substance may undergo a chemical reaction, a transition, or a crystallization. These phenomena involve a heat effect, the magnitude of which may be measured by a differential thermocouple assembly whereby the difference in temperature between the substance under investigation and some inert substance is found. The temperature at which the change occurs serves as a qualitative identification of the substance undergoing the change, and the magnitude of the heat effect serves as a quantitative measure of the amount of the substance present. Using these principles, a method of qualitative and quantitative analysis termed differential thermal analysis has been developed. The method is quite general and has been used for a wide variety of substances. A bibliography of work on differential thermal analysis to the end of 1950 is available (7).

This paper describes an apparatus for differential thermal analysis which was built at the University of Saskatchewan. Some of the results obtained in an investigation of the mineralogical content of some Saskatchewan clays and volcanic ashes are given.

<sup>1</sup>Manuscript received in original form October 29, 1953, and, as revised, September 6, 1955.

<sup>2</sup>Contribution from the Ceramic Department and from the Chemistry Department, University of Saskatchewan, Saskatoon, Saskatchewan, with financial assistance from the Saskatchewan Research Council.

<sup>3</sup>Ceramic Engineer, Industrial Minerals Division, Department of Mines and Technical Surveys, Ottawa; formerly Special Lecturer in Ceramic Engineering and a graduate student in the Ceramic Department, University of Saskatchewan.

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## APPARATUS

*(a) The Furnace*

The furnace was a horizontal muffle electric furnace (Fig. 1) designed after that of Norton (6). It consisted of a circularly grooved 10 in. alundum tube, 2.4 in. O.D. and 2.1 in. I.D. The heating element was 50.5 ft. of 16 gauge nichrome V wire wound onto the alundum tube. The wound tube was insulated with zonalite, which was held in place by a cylindrical container. This container consisted of a cylinder of galvanized iron 11.5 in. in diameter and 10 in. long. The ends were each constructed of four sheets of 3/16 in. transite around whose edges the galvanized iron casing fitted. Each end had a circular hole of the same diameter as the inside of the alundum tube. The furnace was supported by legs made of transite which were bolted to the ends of the furnace. These legs rested on a sheet of transite, which in turn rested on a wooden frame serving as a stand for the furnace.

*(b) The Sample Holder Assembly and the Thermocouples*

Briefly, this unit (Fig. 1) consisted of the following parts. Firstly there were two containers in one of which was placed the sample being investigated and in the other the inert reference substance. The junctions of the differential thermocouple assembly were placed in these containers, one junction in each. Secondly there was a third container filled with the inert substance into which the junction of another thermocouple was inserted. This thermocouple enabled

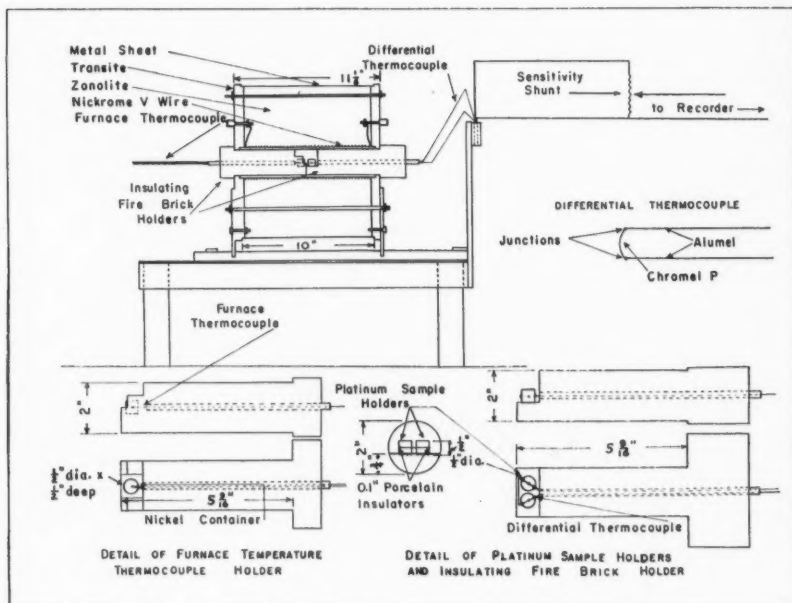


FIG. 1. Cross section of differential thermal analysis furnace.



the temperature of the furnace to be found. Thirdly there were insulating firebrick holders which held the three containers in reproducible positions within the furnace.

Several different types of containers for the sample and the inert substance were tried before a satisfactory type was found. Initially a heavy nickel block patterned after that of Norton (6) was tried. Nickel was used because of its high thermal conductivity and its resistance to corrosion at elevated temperatures. In general, the thermograms obtained using this unit were unsatisfactory, mainly because of lack of sensitivity. It was thought that this unsatisfactory performance was due to the fact that the heat capacity of the block was much greater than that of the sample.

Several workers (3, 4, 9) have successfully used containers with relatively small heat capacities, and the remainder of the containers tried were of this type.

Following the method of Herold and Planje (4), two separate cylinders, one for the sample and the other for the inert material, were assembled in such a manner that they formed the differential thermocouple. To accomplish this the top half of each cylinder was made of alumel, the lower half of chromel. Satisfactory thermograms were not obtained, mainly because of large variations in the base lines of the thermograms. This variation was perhaps due to electrical asymmetry of the sample holder as a result of faulty construction.

The sample and inert material containers finally were made of 0.002 in. thick platinum foil. They were each in the shape of a cylinder, 1/2 in. in diameter and 1/2 in. high. Two pieces of platinum were used to construct each container, a circular piece for the bottom and a rectangular piece for the side. These two pieces were welded together using a steel cylinder as a form. Circular lids were made from platinum foil of the same thickness. Two holes, 0.1 in. in diameter and 180° apart, were located half way down each cylinder. Thin-walled porcelain insulators just long enough to be cemented into the holes were used to insulate the 28 gauge chromel-alumel differential thermocouple wires from the metal cylinders. The cement used was made by mixing alundum cement with a small amount of sodium silicate. The total weight of each sample holder and lid was approximately 1.3 grams.

The furnace temperature was obtained from a 22 gauge chromel-alumel thermocouple whose junction was centered in a nickel cylinder filled with an inert material. The nickel cylinder was 1/2 in. in diameter, 1/2 in. deep, and had walls 1/32 in. thick. A lid of the same thickness was placed on this unit during operation. The nickel cylinder was used for this purpose because of its sturdy construction.

An insulating firebrick cylinder was designed to hold the platinum cylinders in place in the furnace. The part of the cylinder designed to fit into the alundum tube of the furnace was 2 in. in diameter. The outer end of the holder was enlarged to act as a positioning stopper. The inner end was so fashioned that the two cylinders sat directly on the refractory at right angles to the longitudinal axis of the furnace. Two shallow wells, 1/32 in. deep, were in the refractory to



position the platinum cylinders. The positions of the platinum cylinders in the furnace were such that they were centrally located, both vertically and horizontally. A circular hole large enough to contain a two-hole porcelain insulator was drilled through the center of the holder in the longitudinal direction to carry the differential thermocouple leads out of the furnace.

The nickel cylinder used to obtain the furnace temperature was located on a holder similar to the one described above. This holder was positioned at the opposite end of the furnace to the end used for the holder of the platinum cylinders. The inner ends of the two holders butted together so that all three cylinders were brought quite close to one another.

(c) *The Temperature Recorder*

A Leeds and Northrup "Speedomax" two-point strip chart recorder was used to record both the furnace temperature and the differential thermograms. The scale for the former was graduated from 0 to 1200°C. The scale for the latter varied from 0 at the center to 1.5 millivolts on the one side to -1.5 millivolts on the other side. The differential temperatures to which these voltages correspond were often exceeded. To prevent the recorder from going off scale a rheostat whose resistance could be varied from 0 to 25,000 ohms was used as a shunt in the differential circuit. Six settings of the rheostat were calibrated. Hence six scales were available for recording differential temperatures.

(d) *The Regulator for Heat Input to the Furnace*

A 115 volt, 10 amp., 50-60 cycle manually controlled variac was used to regulate the heat input to the furnace. Once a definite heating schedule was devised the temperature control was quite satisfactory.

#### PROCEDURE

The apparatus described above was used to investigate clay minerals and hence the procedure developed was for this type of material. Since this procedure should be applicable to many solids it will be described in detail.

The test materials were allowed to come to equilibrium in a dry room at  $74 \pm 3^\circ\text{F}$ . This temperature was selected in order to obtain the characteristic low temperature absorbed water peaks of the montmorillonites and of halloysite. Representative samples were ground to pass a 100 mesh (Tyler) screen.

Samples were lightly tamped into the platinum container so that it was filled to the top. Ninety mesh pure crystalline alumina obtained from the Norton Company, Worcester, Mass., was used as the inert reference material. It was placed in the other platinum cylinder which was filled to the top. The differential thermocouple junctions were accurately centered in the platinum cylinders during the filling process. After the cylinders had been filled, their position on the holder was carefully checked and the whole assembly was then slid into the furnace.

The furnace temperature was raised by a definite schedule at the rate of 18°C. per minute. Tests were run on an illite and a kaolinite using heating rates of 12°C. and 18°C. per minute. For both minerals more intense and more clearly defined peaks were obtained with the latter rate. For some materials

the sensitivity of the temperature recorder was varied during a run in order to magnify certain reactions more than others. The majority of the curves were carried to 1050°C. However, if a readily fusible material was being investigated the temperature was not allowed to exceed 1000°C. The latter precaution applies to materials such as volcanic ashes, common clays, illites, and some montmorillonites.

The furnace temperature thermocouple was checked periodically by the method suggested by Faust (2). The inversion of  $\alpha$  to  $\beta$  quartz at 573.3°C. was used as a means of calibration. With the type of apparatus used, and with the heating rate employed, the peak due to this reaction occurred at  $572 \pm 2^\circ$  when the sample holder was completely filled with pure quartz. No greater accuracy can be expected, since a temperature range from 0°C. to 1200°C. is crowded into a space of 10 inches on the recorder chart. If any marked deviation occurred from these values, it was taken to be an indication of a defective thermocouple.

On completion of a test the temperatures corresponding to the maximum deflection of the various peaks were noted and compared to those of standard materials. The positions of the peaks served to identify the minerals present. The peak areas per gram of sample were used to estimate quantitatively the amount of each mineral present. Peak amplitudes were not employed since a variation in the heating rate was found to affect the amplitude more than the area. For mixtures it was found that the peak area resulting from a given amount of one constituent was influenced somewhat by the presence of other materials. It was therefore necessary to construct calibration curves from thermograms of synthetic mixtures of known compositions.

To obtain consistent results the following procedure was used to measure the peak areas. The beginning and the end of a peak were defined (6) as the points at which the thermogram started to deviate from the base line. These two points were joined by a straight line and the area enclosed by this line and the part of the thermogram cut off by it was taken to be the peak area and was measured with a planimeter. The method of establishing the high temperature limit of a kaolinite peak for a Saskatchewan clay is illustrated in Fig. 2.

For the ball clays, which contained a large amount of carbonaceous material, the lower limit of the 600°C. kaolinite peak was indefinite. To obtain consistent

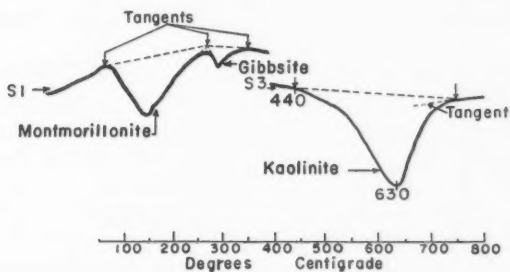


FIG. 2. Resolution of the peak areas of Saskatchewan ball clay 11S-1.

results the above procedure was modified by arbitrarily taking as the lower limit of the peak a point  $190^{\circ}\text{C}$ . lower than the temperature at which maximum deflection occurred. This modification was used for all materials containing kaolinite. An illustration of the use of this procedure is also shown in Fig. 2.

In some instances two peaks occur so close together that they interfere with one another and if the usual method of finding peak areas were followed the areas obtained would be too small. An example of such an interference is illustrated in Fig. 2 where the thermogram of a Saskatchewan ball clay shows that the endothermic peak at  $150^{\circ}\text{C}$ . due to montmorillonite was not finished before the start of the  $300^{\circ}\text{C}$ . endothermic gibbsite peak. Also illustrated in Fig. 2 is the method (6) used to allow for this interference when determining peak areas.

### RESULTS AND DISCUSSION

The results obtained with the apparatus have been given in detail elsewhere (1). Only a few of them will be given here to illustrate what may be expected from an apparatus of this type. In Figs. 3, 4, and 5, respectively, are shown thermograms of the standards of the kaolinite group, of some of the non-clay minerals, and of some Saskatchewan ball clays. Endothermic reactions are represented by peaks pointing down and exothermic reactions by peaks pointing up. A break in a thermogram shows that the scale sensitivity has been changed. The sensitivity is inversely proportional to the scale numbers on the thermograms.

A brief discussion of the thermograms shown in Fig. 5 will be given. Each thermogram shows a prominent endothermic peak in the temperature range  $605^{\circ}$  to  $645^{\circ}\text{C}$ . and an exothermic peak at  $970^{\circ}$  to  $990^{\circ}\text{C}$ . both of which are due to the presence of kaolinite. The small endothermic peak at  $150^{\circ}\text{C}$ . is due to the presence of calcium montmorillonite. The broad exothermic peak in the temperature range  $300^{\circ}$  to  $350^{\circ}\text{C}$ . is due to the presence of organic material and other oxidizable substances. The small sharp endothermic peak at a temperature of  $300^{\circ}\text{C}$ . is attributed to the presence of gibbsite. The presence of goethite would give a peak in the same temperature range. However, if the peak is due to goethite, the iron content of the clays would be higher than that shown by chemical analysis. An example of the quantitative results obtained is given in Table I where for both quartz and alumina the quantities calculated from the mineral contents found by differential thermal analysis for some Saskatchewan ball clays are compared with those found by chemical analysis.

It is rather difficult to estimate the accuracy of the quantitative results. For kaolinite analysis it is thought that for clays containing a high portion of kaolinite the results are within 7 to 12% of the correct value. For the lower grade ball clays, fire clays, and stoneware clay, the kaolinite results are probably within 15% of their correct values. It is estimated that the quartz results are accurate to within 5 to 10% when the quartz content is above 40%. They are thought to be within 10 to 15% when the quartz content is between 40 and 20%. For quartz contents below 20% the results may deviate as much as 15

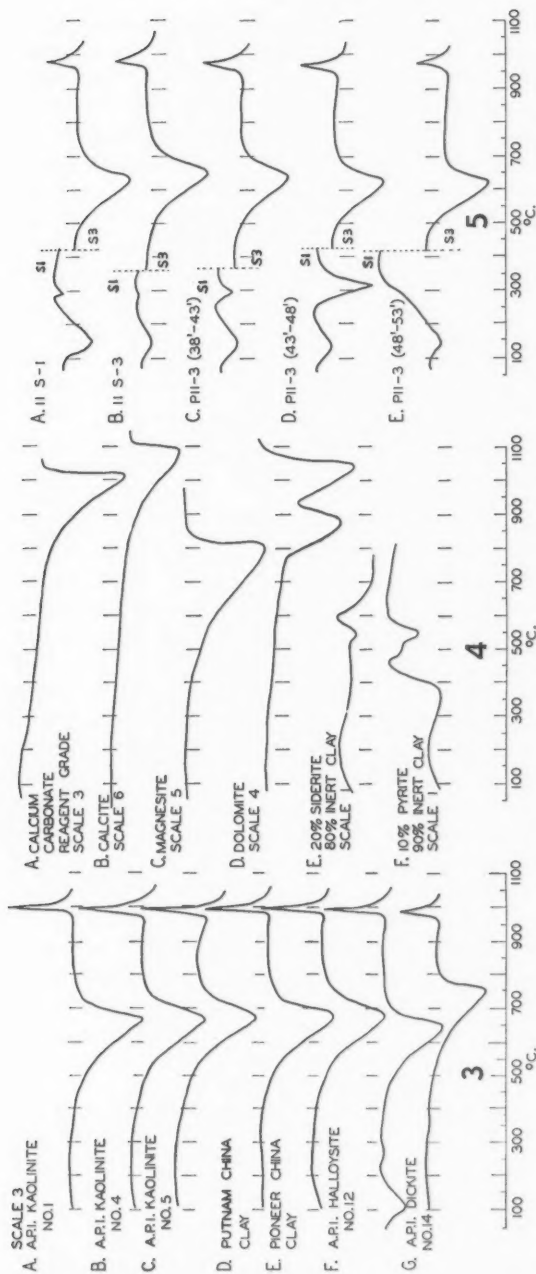


FIG. 3. Thermograms of the standards of the kaolinite group. FIG. 4. Thermograms of some non-clay minerals. FIG. 5. Thermograms of some Saskatchewan ball clays.

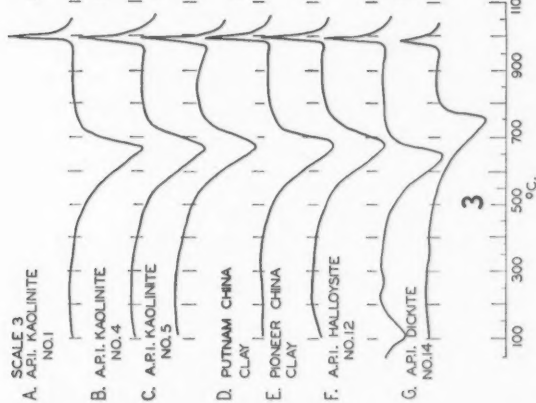
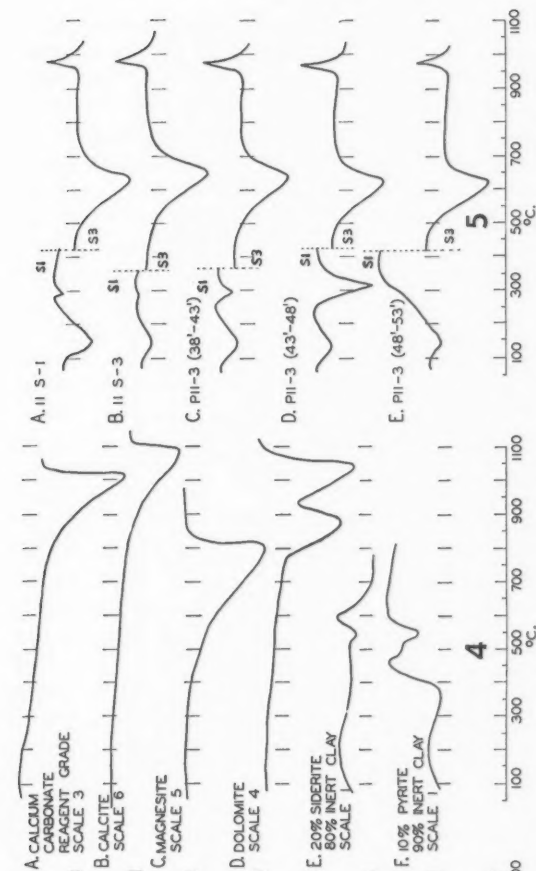


TABLE I  
A COMPARISON OF THE TOTAL  $\text{Al}_2\text{O}_3$  AND  $\text{SiO}_2$  OBTAINED BY DIFFERENTIAL THERMAL ANALYSIS AND BY CHEMICAL ANALYSIS OF SOME  
SASKATCHEWAN BALL CLAYS

Clay sample number	Kaolinite		Montmorillonite		Gibbsite		Quartz		Total		Chemical		Difference	
	2	3	4	5	6	7	8	9	10	11	12	13	between chemical analysis and D.T.A.	
	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	Col. 10 minus Col. 8	Col. 11 minus Col. 9		
10S-1	22.7	19.5	5.4	2.1	1.8	19.6	47.7	23.4	54.21	29.03	+6.5	+5.6		
10S-3	24.4	20.9	3.7	1.4	Trace	23.8	51.9	22.3	57.23	26.29	+5.3	+4.0		
11S-1	22.6	19.4	7.3	2.9	0.7	20.7	50.6	23.0	56.30	27.21	+5.7	+4.2		
11S-3	25.1	21.5	4.0	1.5	Trace	21.4	50.5	23.0	56.24	27.38	+5.7	+4.4		
15S-3	17.9	15.8	7.7	2.9	—	25.2	50.8	18.7	58.28	23.83	+7.5	+5.1		

\*D.T.A.—Differential thermal analysis.

to 20% from the correct values. The quantitative results for montmorillonite are only approximate as all the peaks due to this mineral were obscured except the low temperature endothermic one and the small 950°C. dip. As a qualitative check on the differential thermal analysis results X-ray diffraction patterns were taken of some of the clay samples. There was good agreement for the presence or absence of illite, kaolinite, gibbsite, quartz, and dolomite. There was also agreement where large quantities of montmorillonite were present. However, for some clays differential thermal analysis indicated the presence of small quantities of montmorillonite whereas their X-ray diffraction patterns failed to indicate the presence of this mineral. The method of MacEwan (5) was used in which the montmorillonite lattice is expanded with glycerol before the X-ray diffraction patterns are taken. Control experiments indicated that the sensitivity of the X-ray diffraction method was approximately the same as the amount of montmorillonite indicated by the differential thermal analysis. A further complication is that it has been shown by Speil (8) that very finely ground kaolinite may have an adsorbed water peak at approximately 150°C. Hence for these clays it is very difficult to decide if montmorillonite is present.

In spite of the difficulties involved in the differential thermal analysis of heterogeneous clays, and of the seemingly low accuracy obtained, the method proved to be an excellent one for a rapid determination of the mineralogical composition of Saskatchewan clays and volcanic ashes. One has only to consider the time involved in performing the analysis of clay by chemical means to appreciate the time and expense saved by differential thermal analysis. Furthermore, the apparent advantage of the higher accuracy of the chemical method is lost to a certain extent when it is realized that this higher accuracy is for the total amount of a constituent that is present and not for the various clay minerals present. For example, while the total silica and total alumina percentage may be known quite accurately for a clay, estimating how these are distributed among the various minerals present introduces some rather large uncertainties into the final results for the mineralogical composition.

#### ACKNOWLEDGMENTS

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## THE DECOMPOSITION, OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

### XXVIII. THE THERMAL DECOMPOSITION OF *n*-PENTANE AS AFFECTED BY THE FLOW CONFIGURATION IN KING REACTOR NO. 10<sup>1</sup>

BY H. SHANFIELD<sup>2</sup> AND R. O. KING<sup>3</sup>

#### ABSTRACT

The thermal decomposition of *n*-pentane in a nitrogen atmosphere in the flow system of the King Reactor No. 10 has been investigated over the temperature range 647°C. to 727°C. The flow configuration in this reactor is such that an approach to the true reaction temperature can be obtained by successive increases in the rate of heat transfer. The apparent reaction order is unity, and the extrapolated energy of activation  $34,000 \pm 2000$  calories per gram mole. Velocity constant data are fitted by the expression  $\log_{10} k = 7.8 - (34,000/2.3 RT)$ . The low activation energy may be due in part to catalysis by the Vycor surfaces. A Rice free-radical mechanism can account for the reaction products quantitatively and qualitatively. On this basis the relative chance of reaction of free radicals with primary and secondary hydrogens in the *n*-pentane molecule is 1:6 respectively.

#### INTRODUCTION

An investigation of reaction kinetics in flow systems is usually accompanied by some uncertainty in respect of the temperature of the reaction. Reactor No. 10, which incorporated a novel flow configuration, was first used for oxidation reactions, Part I (2). Its design is such that reaction temperature can be estimated with a fair degree of accuracy. *n*-Pentane was decomposed thermally in the reactor in order to obtain velocity constant data in a sparsely explored temperature region and an estimate of the activation energy of the reaction. The thermal decomposition of pentane was of interest because of the reactions that occur when mixtures with air are ignited by the heat of compression in an Otto cycle engine.

#### EXPERIMENTAL ARRANGEMENTS

A pentane-nitrogen mixture was used for the experiment. The rate of supply of nitrogen was always 300 cc./min. and *n*-pentane concentration was maintained at 0.0219 mole fraction, except when reaction order determinations were made. It was then varied from 0.0219 to 0.00365 mole fraction.

The reactor design is illustrated by Fig. 1. It will be seen that an inverted cup was formed in the end of a Vycor glass tube having an external diameter such that an annulus 1.0 mm. wide was formed between it and a concentric outer tube, also of Vycor. A transite washer fitted tightly in the outer tube formed the base of the reaction space. The washer was provided with a central opening through which the pentane-nitrogen mixture was admitted as a stream-

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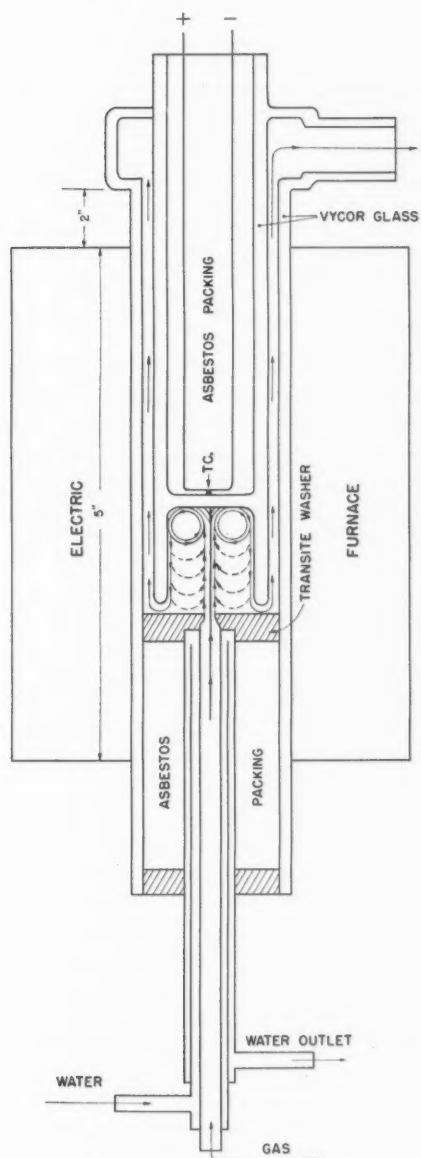


FIG. 1. King reactor No. 10.

line jet issuing from an orifice in the end of a water cooled inlet device. The jet impinged on the horizontal surface of the cup and produced a flow configuration which comprised a toroidal vortex in the *upper* end of the cup. It was expected therefore that reaction rate would not appreciably be affected by the transite washer which moreover attained a somewhat lower temperature because it did not provide complete thermal insulation between the upper and the cooler lower part of the reactor. Experiments were however carried out with a reactor constructed entirely of Vycor. The results of these were not different from those obtained when the transite washer was used and cleaning was difficult because the sole access to the reaction space was through the small hole provided for the orifice of the water cooled mixture inlet. Cleaning was accomplished easily when a removable transite washer was fitted in the reactor and this arrangement was used for all of the experiments described in this paper.

The reaction space included the volumes of the cup and of a length of the annular space. It was found by separate experiments that reaction occurred at an appreciable rate in a length of 6 cm. of the annular passage from the cup to the exit. The total volume of reaction space was estimated accordingly to be 5.6 cc. The time of residence of the mixture in the reaction space, if based on an average temperature of 750°C., was therefore 0.33 sec., approximately.

The kinetic energy supplied to the toroidal vortex by the jet of reacting mixture is absorbed mainly by surface friction; a factor which determines rate of heat transfer. In accordance with this view, the rate of heat transfer may be taken as proportional to the kinetic energy in the jet. Orifices 2.0, 1.0, 0.5, and 0.25 mm. in diameter were used for the experiment. The kinetic energy supplied accordingly to the toroidal vortex varied with the square of the velocity of the jet and this velocity varied inversely with the square of the diameter of the orifice. Thus when orifice diameter was reduced from 2.0 to 0.25 mm., and rate of mixture supply remained unchanged, the rate of supply of kinetic energy to the vortex increased 64-fold and the rate of heat transfer from the *surface in contact with the vortex* tended to increase in the same proportion.

Temperatures as measured by the thermocouple, Fig. 1, were taken as indicated reaction temperatures. They were varied over the range 650°C. to 750°C. When steady temperatures were established a sample of the effluent gas was bled off the system without a disturbance of the pressure. Decomposition data and product analyses were obtained accordingly at intervals of 10°C. when each of the four orifices were used. In addition, a limited series of experiments was made to determine heat transfer characteristics.

Fig. 2 is a schematic diagram of the over-all apparatus used. Cylinder nitrogen was passed through a purifying train to remove oxygen, carbon dioxide, and water. *n*-Pentane (99% purity) was delivered to the nitrogen at the required rate by means of a microdoser *M*, a device previously described (3). The mixture entered the electrically heated reactor where decomposition occurred. The reaction products were subsequently analyzed by fractional distillation in the LeRoy still (4), in conjunction with the Toepler pump and a constant volume burette. Hydrogen was determined by diffusion through a hot palladium tube. In addition, analyses were confirmed by mass spectrometer.

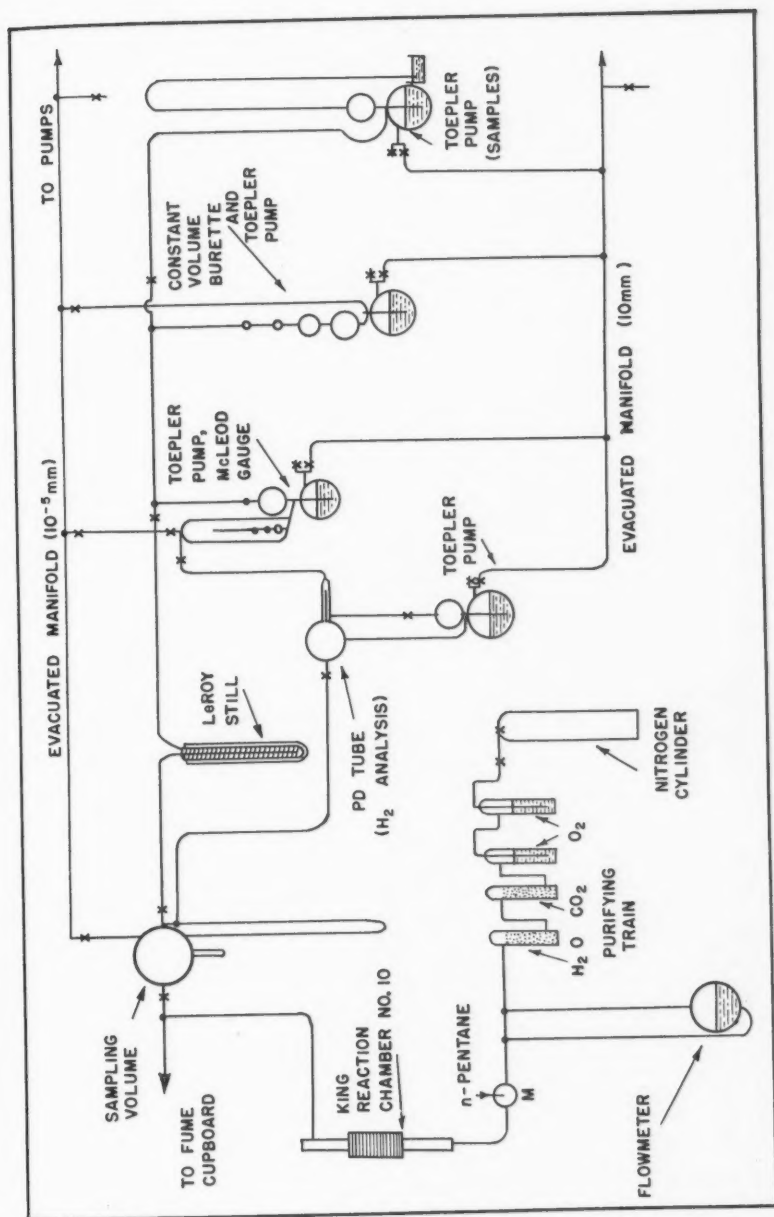


Fig. 2. Arrangement of apparatus.

## RESULTS AND DISCUSSION

In Fig. 3 the percentage conversion of *n*-pentane to other products is plotted against inlet orifice diameter, for temperatures as indicated by the thermocouple, ranging from 650°C. to 750°C. When the temperature is maintained

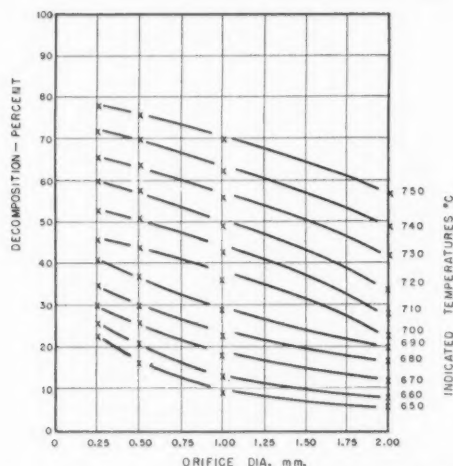


FIG. 3. Rate of decomposition at indicated temperatures ranging from 650°C. to 750°C. as related to orifice diameter.

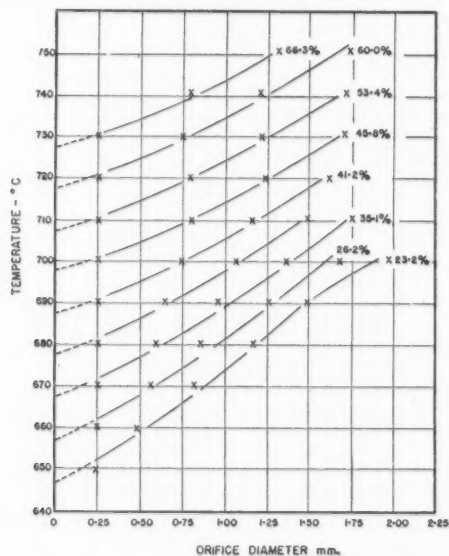


FIG. 4. Relationship between orifice diameter and the indicated temperature required for constant rates of decomposition ranging from 23% to 66%.

constant, decomposition decreases with increasing orifice size. These data are replotted in Fig. 4 for various constant degrees of conversion. This shows that the thermocouple temperature required to bring about a certain percentage decomposition decreases with decreasing orifice diameter. This effect appears to arise from the superior heat transfer rates obtained when the kinetic energy supplied to the vortex in the reactor increases with an increase in jet velocity. It is assumed that the temperatures to which these curves tend at zero diameter orifice are the true reaction temperatures.

Reaction temperatures could have been raised to the degree required for a higher rate of decomposition than the maximum of 78%, attained when the indicated temperature was 750°C. and the mixture was admitted through the 0.25 mm. diameter orifice. This, however, would have produced a larger proportion of  $H_2$ ,  $CH_4$ , and carbon in the products. The rate of carbon formation was negligible in the conditions used for these experiments, the carbon that was formed appearing only as a darkening of the cool end of the reactor, after long continued use.

Reaction velocity constants have been calculated from the decomposition data by the use of Benton's equation for reactions taking place at constant pressure in flow systems (1). Activation energies were estimated in the usual way from a plot of  $\log_e k$  against  $1/T$ ,  $T$  being absolute temperature in °K. Fig. 5 shows such a plot for the data resulting from extrapolation to zero diameter orifice. A straight line is obtained whose slope yields an energy of activation of 34,000 calories per gram mole for the reaction. Fig. 6 is a plot of the apparent activation energies calculated from the decomposition-temperature data for each orifice diameter, as well as the extrapolated value. The S-

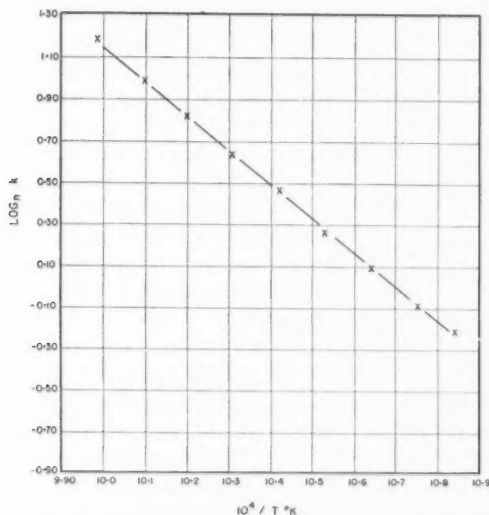


FIG. 5. Extrapolation to zero diameter orifice temperature range 647° to 727°C.

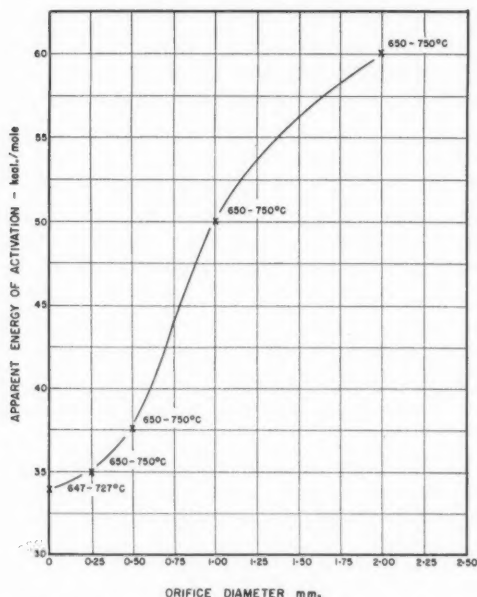


FIG. 6. Apparent energy of activation as related to orifice diameter, temperature ranges as shown.

shaped curve ranges from 60,000 to 34,000 calories per gram mole, from a relatively low rate of heat transfer case to the ideal one. The extremely low activation energy found in this work points to possible catalysis by the reactor surfaces. A preliminary experiment in which the reactor annulus was packed with Vycor fibers has shown a significant increase in reaction rate.

Flow methods are not generally used for studies of reaction kinetics and reactor No. 10 differs from the conventional type in that the flow configuration in it incorporates a toroidal vortex in addition to the laminar flow to be expected in a narrow annulus. In the light of results for oxidation reactions in reactor No. 10 given by King in Part II (2), unusual kinetic effects are to be expected because of the enhancement of heterogeneous reactions. Thus when the reactor is used for a study of decomposition reactions relatively low values for activation energy and the pre-exponential factor might well be expected.

Heat transfer data are plotted in Fig. 7. This figure is a plot of indicated temperature against orifice diameter for a constant electrical power input. The broken line, graph (3), shows the temperature condition when no gases pass through the reactor. When nitrogen alone is admitted at the usual flow rate, graph (2) is obtained. When pentane is added to the nitrogen, graph (1) is obtained. There is a successive drop in thermocouple temperature as orifice diameter is decreased, owing to increasing heat transfer rate, and the gas temperature approaches the indicated temperature. It appears reasonable to assume that extrapolation to zero diameter orifice would yield the true gas

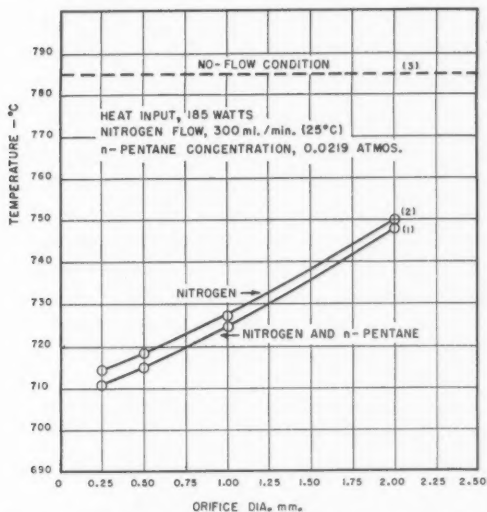


FIG. 7. Indicated temperature for a constant rate of heat input as affected by orifice diameter.

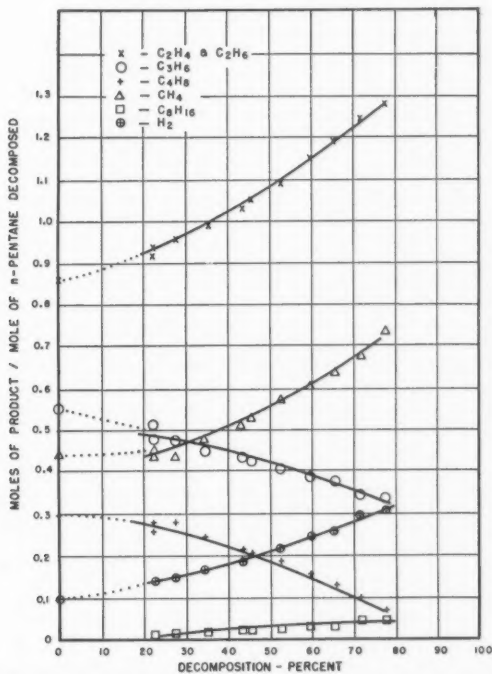


FIG. 8. Product selectivities as affected by the degree of decomposition.



temperature, and the results given by the graphs in Fig. 4 were obtained accordingly. The difference between graphs (2) and (1) is due to the endothermicity of the decomposition reaction.

#### REACTION MECHANISM

Analyses of reaction products are shown by the graphs of Fig. 8. Ethylene-ethane, propylene, butene-1, unreacted *n*-pentane, and the octenes were determined directly by fractional distillation. Methane was estimated by difference from the carbon-hydrogen balance. The absence of propane was confirmed by mass spectrometer analysis. In agreement with previous data, the moles of a particular product per mole of hydrocarbon decomposed i.e. the selectivity seems to depend upon the degree of decomposition rather than the temperature at which it was attained. It is for this reason that temperature does not appear as a variable on this figure.

The data are replotted on a different basis, Fig. 9. For this purpose the following mechanism is postulated:

- (1)  $C_5H_{12} \rightarrow 2C_2H_4 + CH_4$
- (2)  $C_5H_{12} \rightarrow C_2H_6 + C_3H_6$
- (3)  $C_5H_{12} \rightarrow C_2H_4 + C_3H_6 + H_2$
- (4)  $C_5H_{12} \rightarrow C_4H_8 + CH_4$
- (5)  $C_2H_4 \rightarrow \frac{1}{2}C_8H_{16}$

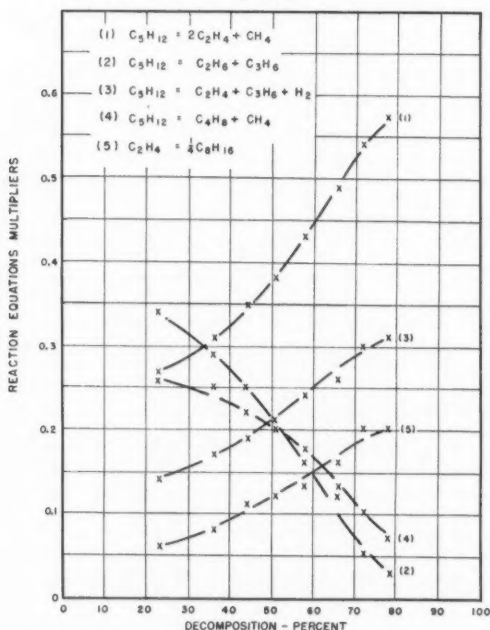
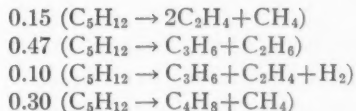


FIG. 9. Reaction equation multipliers as affected by per cent decomposition temperature range, 650° to 750°C.

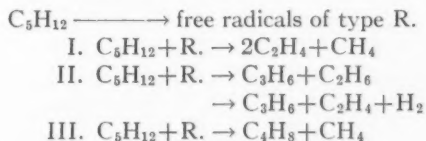
The ordinates of the figure represent multipliers which must be applied to these equations to fit the results; abscissae are per cent decomposition. When the data of both Figs. 8 and 9 are extrapolated to 0% decomposition, the following product composition is obtained:

Components	Moles/mole <i>n</i> -pentane decomposed
$C_2H_4 + C_2H_6$	0.87
$C_3H_6$	0.57
$C_4H_8$	0.30
$H_2$	0.10
$CH_4$	0.45 (by difference)
	<hr/>
Total	2.29

Presumably these are the primary products of decomposition of *n*-pentane under these experimental conditions. Similarly the primary reaction equations are:



The Rice free-radical mechanism postulates the following series of reactions for the thermal decomposition of *n*-pentane:



Reaction I results from the free radical R. attacking the 1-position hydrogen, II by the attack of the 2-position secondary hydrogen, and III by attack of the 3-position secondary hydrogen. Rice assumed (5) that the chance of reaction of R. with primary and secondary hydrogens in the hydrocarbon molecule was 1:2 respectively. In the present work the chances of reaction of R. with 1, 2, and 3-position hydrogen atoms in the *n*-pentane molecule are:

$$\frac{0.15}{6} : \frac{0.47+0.10}{4} : \frac{0.30}{2} \text{ or } 1 : 5.7 : 6.$$

That is, the present work points to a ratio of 1:6 instead of 1:2. This high ratio may be related to some catalytic effect of the surface.

#### REACTION ORDER

The apparent reaction order was inferred from experiments in which the initial *n*-pentane concentration was varied. The results are shown in Fig. 10. The data show essentially no change in degree of conversion for a large change

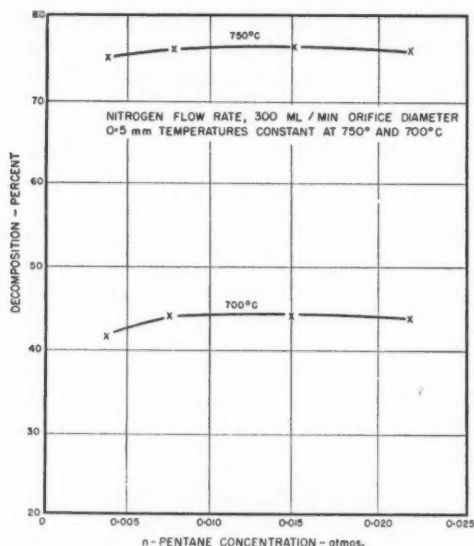


FIG. 10. Per cent decomposition as affected by reactant concentration.

in *n*-pentane concentration, which is one of the criteria of a first order reaction. This of course does not detract from the possibility that the reaction is catalytic.

#### ACKNOWLEDGMENT

The experimental work was carried out in the Department of Chemical Engineering, University of Toronto, with the co-operation of Professor R. R. McLaughlin, Head of the Department. The cost of the work was defrayed in part by a grant from the Defence Research Board, Ottawa. Generous co-operation was received from Professor D. J. LeRoy of the Department of Chemistry, University of Toronto, and Mr. S. Sandler, Defence Research Board Scientific Officer. The authors are indebted to the Chairman of the Defence Research Board for permission to publish.

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## ESTERS OF FLUOROACETIC ACID AND OF 2-FLUOROETHANOL<sup>1</sup>

BY F. L. M. PATTISON, R. R. FRASER, E. J. MIDDLETON,  
J. C. SCHNEIDER, AND J. B. STOTHERS

### ABSTRACT

Esters of fluoroacetic acid and of 2-fluoroethanol have been prepared by standard procedures, and their physical constants tabulated. The long carbon chains did not increase the toxicity of the fluorine-containing moieties. Several of the members have shown outstanding activity as systemic insecticides.

A pronounced alternation in toxicity of members of the ascending homologous series of  $\omega$ -fluorocarboxylate esters,  $F(CH_2)_nCOOR$ , and of  $\omega$ -fluoroalcohols,  $F(CH_2)_nCH_2OH$ , has been reported (3, 11). It has been established that if  $n$  is odd, the compounds are toxic and produce symptoms in animals similar to those produced by fluoroacetic acid, whereas if  $n$  is even, the compounds are devoid of toxic properties. In other words, those compounds containing an even number of carbon atoms are toxic, whereas the odd-numbered members are innocuous. This alternation in toxicity has been correlated with the  $\beta$ -oxidation theory of the breakdown of long-chain carboxylic acids in the animal body (14). Clearly, the even-numbered members would yield the toxic fluoroacetic acid in all cases, whereas the odd-numbered members would be oxidized only so far as the non-toxic 3-fluoropropionic acid.

In both the above series, the toxicity of those compounds in which  $n$  is odd increases markedly with ascent of the series. This is contrary to expectation; on the basis of the  $\beta$ -oxidation theory, the toxicity should decrease because of the increasing chain which must first be oxidized before fluoroacetic acid is produced. One explanation of this anomalous toxicity pattern was that the higher members might have a greater fat : water distribution coefficient (3, 18); this would result in a more rapid passage through the cell membrane, with subsequent breakdown giving a higher intracellular concentration of the toxic principle.

As a possible means of verifying this idea, various long-chain esters of fluoroacetic acid and of 2-fluoroethanol were prepared. It was argued that if these esters were preferentially absorbed at the site of activity because of the long chain, they should show a toxicity comparable to that of the extremely toxic higher members of the  $\omega$ -fluorocarboxylate and  $\omega$ -fluoroalcohol series. However the compounds proved to be much less toxic than methyl fluoroacetate (Table I), suggesting that hydrolysis of the ester had probably occurred before the increased fat-solubility had had time to exert its effect.

<sup>1</sup>Manuscript received October 17, 1955.

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TABLE I  
TOXICITY OF CERTAIN ESTERS OF FLUOROACETIC ACID AND OF 2-FLUOROETHANOL

Ester	L.D. <sub>50</sub> for mice (mgm./kgm.)
Methyl fluoroacetate (for comparison)	8.2
Undecyl fluoroacetate	60
Lauryl fluoroacetate	30
2-Fluoroethyl caproate	>96
2-Fluoroethyl laurate	32
2-Fluoroethyl oleate	200

These preliminary results were completed in 1950, and at that time the possible value of these esters as insecticides was recorded (10).

Schrader has described the powerful activity as contact and systemic insecticides of various derivatives of 2-fluoroethanol (21, 22); more recently, David has reported (4) that sodium fluoroacetate is effective as a contact and systemic insecticide, but that its hazardous nature precludes its use on a commercial scale. Since the esters of 2-fluoroethanol and fluoroacetic acid described in this paper are related structurally to the compounds tested by Schrader and by David, and yet are much less toxic to mammals, representative members were sent to Dr. H. Hurtig, Entomology Section, Suffield Experimental Station, Ralston, Alberta, for testing as candidate insecticides. The promising preliminary results (8) indicated that both classes of esters were worth studying in more detail; accordingly, from 1950 to 1954, samples of new compounds, selected on the basis of results obtained, were submitted for screening (13).

In the insecticidal testing, most members of both classes of esters displayed strong systemic action, strong fumigant action, and strong contact action. Phytotoxicity was high for the lower members of each class, but only slight for the higher members, while systemic activity diminished with the higher saturated members. The point at which phytotoxicity was low but systemic activity was high represented the compounds of maximum effectiveness, and among these were 2-fluoroethyl laurate, tridecanoate, and oleate (12, 15) and lauryl fluoroacetate. It is hoped that details of the insecticidal results will be published elsewhere in due course.<sup>2</sup>

Glyceryl 1-monofluoroacetate and glyceryl trismonofluoroacetate were prepared for pharmacological studies. Methyl and ethyl fluorothiolacetate were prepared for isolated enzyme studies. A few derivatives prepared as intermediates for other purposes are included in Tables II and III for completeness. The toxicities of these various compounds have been recorded and discussed elsewhere (13).

#### METHODS OF PREPARATION

Most of the preparations described in this paper have been carried out only once, and sometimes on a very small scale; hence the yields quoted are not necessarily the highest obtainable.

<sup>2</sup>A preliminary report, by H. Hurtig and F. L. M. Pattison, is in preparation.

TABLE II  
ESTERS OF FLUOROACETIC ACID

Compound	Formula	Yield, %	Melting point or boiling point °C.	$n_D^{25}$ mm.	Analytical results					
					C %		H %		Other %	
					Calc.	Found	Calc.	Found	Calc.	Found
1. Octyl fluoroacetate <sup>a</sup>	$\text{FCH}_2\text{COO}(\text{CH}_2)_7\text{CH}_3$	96	103-105	9	1.4165	63.16	63.40	10.00	10.15	
2. Decyl fluoroacetate <sup>b</sup>	$\text{FCH}_2\text{COO}(\text{CH}_2)_9\text{CH}_3$	95	128-130	9	1.4240	66.06	66.24	10.54	10.46	
3. Undecyl fluoroacetate	$\text{FCH}_2\text{COO}(\text{CH}_2)_{10}\text{CH}_3$	76	97-97.5	0.5	1.4269	67.23	67.32	10.77	10.52	
4. Undecylenyl fluoroacetate	$\text{FCH}_2\text{COO}(\text{CH}_2)_9\text{CH}_2\text{CH}_2$	48	132-134	4	1.4356					F, 8.04
5. Lauryl fluoroacetate <sup>c</sup>	$\text{FCH}_2\text{COO}(\text{CH}_2)_{11}\text{CH}_3$	88	146-150	4	1.4294	68.29	68.39	10.97	10.98	
6. Myristyl fluoroacetate <sup>d</sup>	$\text{FCH}_2\text{COO}(\text{CH}_2)_{13}\text{CH}_3$	78	166-171	9	1.4334	70.06	70.17	11.32	11.08	
7. Cetyl fluoroacetate	$\text{FCH}_2\text{COO}(\text{CH}_2)_{15}\text{CH}_3$	36	m.p. 32-33°							F, 6.32
8. Octadecyl fluoroacetate	$\text{FCH}_2\text{COO}(\text{CH}_2)_{17}\text{CH}_3$	38	m.p. 41-42°							F, 5.98
9. Phenyl fluoroacetate <sup>e</sup>	$\text{FCH}_2\text{COOC}_6\text{H}_5$	47	m.p. 60-61°							
10. Allyl fluoroacetate <sup>f</sup>	$\text{FCH}_2\text{COOCH}_2\text{CH}=\text{CH}_2$	67 <sup>g</sup>	136-137	750	1.4030					
11. 2,3-Dibromopropyl fluoroacetate	$\text{FCH}_2\text{COOCH}_2\text{CHBrCH}_2\text{Br}$	83	135-136	13	1.5053	21.59	21.61	2.52	2.49	Br, 57.55 Br, 57.51
12. Methyl fluorothiolacetate <sup>g</sup>	$\text{FCH}_2\text{COSCH}_3$	56	119-120	740	1.4565	33.34	33.24	4.63	4.73	S, 20.63 S, 20.46
13. Ethyl fluorothiolacetate	$\text{FCH}_2\text{COSC}_2\text{H}_5$	70	135-136	740	1.4525	39.34	39.49	5.73	5.86	S, 26.23 S, 26.15
14. Fluoroacetyl isopropylideneglycerol	$\text{FCH}_2\text{COOCH}_2\text{CHO} \begin{array}{c} \diagup \text{C}(\text{CH}_3)_2 \\   \\ \text{CH}_2\text{O} \end{array}$	81	87-89	2	1.4253	50.00	50.14	6.77	6.74	
15. Glyceryl 1-mono-fluoroacetate	$\text{FCH}_2\text{COOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$	94	163-165	2	1.4372	39.47	39.28	5.97	5.98	
16. Glyceryl trismono-fluoroacetate <sup>h</sup>	$\text{C}_3\text{H}_5(\text{OCOCH}_2\text{F})_3$	38	206-208	13	1.4272	39.75	39.79	4.05	4.08	

<sup>a</sup>Bergmann and Blank (2) report b.p. 223° and  $n_D^{20}$  1.417; Kitano, Fukui, Nozu, and Osaka (9) report b.p. 87° at 3 mm. and  $n_D^{20}$  1.4204. <sup>b</sup>Kitano et al. (9) report b.p. 148° at 20 mm. <sup>c</sup>Payne (16) mentions lauryl fluoroacetate, but gives no constants; Kitano et al. (9) report b.p. 131° at 3 mm. and  $n_D^{20}$  1.4330. <sup>d</sup>Kitano et al. (9) report b.p. 175° at 6 mm. <sup>e</sup>Saunders and Stacey (19) report m.p. 63.5-64°. <sup>f</sup>J. Saunders and Stacey (20) report b.p. 136-137° at 760 mm.; Gryszkiewicz-Trachimowski, Gryszkiewicz-Trachimowski, and Levy (5) report b.p. 137-137.5°. <sup>g</sup>Gryszkiewicz-Trachimowski, Sporzynski, and Wnuk (6) report b.p. 142-143°; Kitano et al. (9) report b.p. 140°. <sup>h</sup>Gryszkiewicz-Trachimowski et al. (6) report b.p. 177-179° at 10 mm. <sup>i</sup>Using pyridine, and chloroform as solvent.

TABLE III  
ESTERS OF 2-FLUOROETHANOL

Compound	Formula	Yield, %	Melting point or boiling point °C.	mm.	$n_D^{25}$	Analytical results			
						C %		H %	
						Calc.	Found	Calc.	Found
17. 2-Fluoroethyl valerate	$\text{FCH}_2\text{CH}_2\text{OCO}(\text{CH}_2)_5\text{CH}_3$	59	170-171	750	1.4015	56.75	56.76	8.78	8.82
18. 2-Fluoroethyl caproate	$\text{FCH}_2\text{CH}_2\text{OCO}(\text{CH}_2)_6\text{CH}_3$	70	91-93	24	1.4059	59.27	59.45	9.26	9.27
19. 2-Fluoroethyl caprylate	$\text{FCH}_2\text{CH}_2\text{OCO}(\text{CH}_2)_8\text{CH}_3$	74	110-113	15	1.4159	63.16	63.12	10.00	9.91
20. 2-Fluoroethyl pelargonate	$\text{FCH}_2\text{CH}_2\text{OCO}(\text{CH}_2)_7\text{CH}_3$	67	119-121	12	1.4198	64.71	64.89	10.29	10.38
21. 2-Fluoroethyl caprate	$\text{FCH}_2\text{CH}_2\text{OCO}(\text{CH}_2)_9\text{CH}_3$	91	134-136	14	1.4236	66.06	66.02	10.54	10.67
22. 2-Fluoroethyl laurate	$\text{FCH}_2\text{CH}_2\text{OCO}(\text{CH}_2)_{10}\text{CH}_3$	85	153-155	13	1.4293	68.29	68.28	10.97	10.85
		42 <sup>a</sup>	156-157	17	1.4294				
23. 2-Fluoroethyl tridecanoate	$\text{FCH}_2\text{CH}_2\text{OCO}(\text{CH}_2)_{11}\text{CH}_3$	78	160-162	10	1.4324	69.23	69.49	11.15	11.13
		27 <sup>a</sup>	130-133	1.5	1.4318				
24. 2-Fluoroethyl myristate	$\text{FCH}_2\text{CH}_2\text{OCO}(\text{CH}_2)_{12}\text{CH}_3$	85	170-172	9		70.06	70.27	11.32	11.23
			m.p. 29-29.5°						
25. 2-Fluoroethyl palmitate	$\text{FCH}_2\text{CH}_2\text{OCO}(\text{CH}_2)_{14}\text{CH}_3$	88	m.p. 42-43°			71.53	71.47	11.59	11.65
26. 2-Fluoroethyl stearate	$\text{FCH}_2\text{CH}_2\text{OCO}(\text{CH}_2)_{16}\text{CH}_3$	92	m.p. 49.5-50°			72.73	72.70	11.82	11.79
27. 2-Fluoroethyl oleate <sup>b</sup>	$\text{FCH}_2\text{CH}_2\text{OCCOC}_{17}\text{H}_{33}$	46	169-170	1	1.4488	73.16	73.33	11.28	11.21
28. 2-Fluoroethyl benzoate	$\text{FCH}_2\text{CH}_2\text{OCCOC}_6\text{H}_5$	42	106-108	10	1.4998	64.28	64.13	5.36	5.27

<sup>a</sup> Using *p*-toluenesulphonic acid in place of sulphuric acid. <sup>b</sup> Prepared by R. G. Woolford.



(a) *Esters of Fluoroacetic Acid*

The simple esters of fluoroacetic acid (Compounds 1-9) were prepared from the corresponding alcohols by treatment with fluoroacetyl chloride. Yields, physical constants, and analytical results are shown in Table II. Similarly, the two fluorothiolacetates (Compounds 12 and 13) were prepared from methyl and ethyl mercaptan respectively.

Allyl fluoroacetate was most conveniently obtained from allyl alcohol and fluoroacetyl chloride in the presence of pyridine and using chloroform as solvent. Earlier preparative methods examined in this laboratory included the treatment of allyl alcohol with the following: fluoroacetyl chloride with no solvent (40%); fluoroacetyl chloride using sulphuric acid (30%); fluoroacetyl chloride using *p*-toluenesulphonic acid (30%); and fluoroacetic anhydride using sulphuric acid (26%). Bromine added readily to allyl fluoroacetate to form 2,3-dibromopropyl fluoroacetate, which was required as an intermediate for other work.

Isopropylideneglycerol was fluoroacetylated in 81% yield with fluoroacetyl chloride at room temperature for 48 hr., chloroform being used as solvent. The hydrolysis of this to glyceryl 1-monofluoroacetate (fluoromonoacetin) was accomplished in 94% yield with 10% fluoroacetic acid at low temperature. This synthesis was adapted from the work of Baer and Fischer (1). Glyceryl trismonofluoroacetate was obtained by direct fluoroacetylation of glycerol in benzene as solvent.

(b) *Esters of 2-Fluoroethanol*

The simple 2-fluoroethyl esters (Compounds 17-28) were obtained by esterification of 2-fluoroethanol with sulphuric acid and the appropriate organic acids. Yields, physical constants, and analytical results are shown in Table III.

### EXPERIMENTAL<sup>3</sup>

*Fluoroacetyl Chloride*

Technical sodium fluoroacetate (Monsanto "Compound 1080", containing 90% sodium fluoroacetate), (167 gm., 1.5 moles), previously dried for three days over phosphorus pentoxide, and phthalyl chloride (375 gm., 1.68 moles) were mixed thoroughly and gently heated in a flask fitted for distillation. All the distillate of boiling point up to 90° was collected in a flask protected by a calcium chloride tube. The crude product was redistilled, yielding fluoroacetyl chloride (138 gm., 95%) of b.p. 70-71°. [Saunders and Stacey (19) report b.p. 71.5-73° at 760 mm.]

*Esters of Fluoroacetic Acid (Compounds 1-9)*

The simple esters are represented by the following example:

*n*-Decyl fluoroacetate.—Pyridine (7 gm.) and *n*-decyl alcohol (10.3 gm., 0.065 mole) were mixed in a 100 ml. flask fitted with a dropping-funnel, mechanical stirrer, and reflux condenser, and cooled in an ice bath. Moisture

<sup>3</sup>Physical constants are recorded in Tables II and III.

was rigorously excluded. Fluoroacetyl chloride (10 gm., 0.104 mole) was added dropwise with stirring. After the addition was complete, the mixture was heated on a steam bath for 10 min. The ester was isolated by dilution with water and extraction with ether. After it was washed with dilute sodium carbonate, the ethereal solution of the ester was dried over anhydrous sodium sulphate. After removal of the ether, the residue on distillation gave *n*-decyl fluoroacetate (13.4 gm., 95%), a colorless, pleasant-smelling liquid.

The solid esters were prepared in the same way. They were isolated by dilution with water followed by filtration of the waxy precipitates, and purified by several recrystallizations from ethanol, the solution being cooled very slowly with stirring to avoid the formation of oils. The pure esters were colorless, low-melting solids with faint, pleasant odors.

#### *Allyl Fluoroacetate*

Fluoroacetyl chloride (11.0 gm., 0.114 mole) was added dropwise to a gently agitated mixture of allyl alcohol (12 gm., 0.207 mole) and pyridine (16.4 gm., 0.208 mole) in chloroform (100 ml.). The temperature was maintained at  $-10^{\circ}$  by means of an ice-HCl bath. The mixture was allowed to stand in the bath for four hours after completion of the addition, and then stored for 24 hr. at  $0^{\circ}$ . The mixture was washed twice with dilute hydrochloric acid, twice with 10% sodium bicarbonate solution, and then twice with water. After it was dried over anhydrous sodium sulphate, the product was fractionated through a modified Podbielniak column at atmospheric pressure, yielding allyl fluoroacetate (8.2 gm., 67%).

#### *2,3-Dibromopropyl Fluoroacetate*

Bromine (14.5 gm., 0.091 mole) was added dropwise and with vigorous stirring to a solution of allyl fluoroacetate (10.2 gm., 0.086 mole) in carbon tetrachloride (50 ml.), maintained at  $-10^{\circ}$ . The stirring was continued while the solution was warmed slowly to room temperature. Distillation of the product through a modified Podbielniak column yielded 2,3-dibromopropyl fluoroacetate (19.6 gm., 83%).

#### *Methyl and Ethyl Fluorothiolacetate<sup>4</sup>*

Fluoroacetyl chloride (24 gm., 0.25 mole) was added dropwise and with stirring to the appropriate mercaptan (0.25 mole), cooled in an ice bath. The mixture was allowed to stand at room temperature for 48 hr., and then heated under reflux for one hour. After cooling, the mixture was diluted with water and extracted with ether. The extract was washed successively with aqueous sodium carbonate and with water, and dried over anhydrous calcium chloride. After removal of the ether, the product was fractionated, giving the pure fluorothiolacetate.

#### *Fluoroacetyl Isopropylideneglycerol*

Fluoroacetyl chloride (32.2 gm., 0.3 mole) was added slowly to an agitated solution of isopropylideneglycerol (17, p. 502) (44 gm., 0.3 mole) and pyridine

<sup>4</sup>Prepared by J. E. Millington.

(28 gm., 0.33 mole) in dry ethanol-free chloroform (300 ml.), maintained at  $-10^{\circ}$ . Stirring was continued for two hours after the addition was complete, and the mixture was then allowed to stand at room temperature for two days. The mixture was washed twice with water and dried over anhydrous calcium chloride. The chloroform was removed by distillation at atmospheric pressure, and the residue on fractional distillation yielded fluoroacetyl isopropylideneglycerol (51.2 gm., 81%).

*Glyceryl 1-Monofluoroacetate (Fluoromonoacetin)*

Fluoroacetyl isopropylideneglycerol (8.8 gm., 0.045 mole) and 10% aqueous fluoroacetic acid (45 ml.) were mixed and heated with vigorous stirring at  $60^{\circ}$  ( $\pm 2^{\circ}$ ) until the disappearance of the emulsion. The clear solution was cooled and the unhydrolyzed isopropylideneglycerol was removed by several extractions with petroleum ether ( $30-60^{\circ}$ ). The aqueous solution was concentrated *in vacuo* (8-10 mm.) to a thick syrup, at a bath temperature of  $35^{\circ}$ . This was then warmed at  $35^{\circ}$  at 0.5 mm. for three hours, and finally distilled, yielding glyceryl 1-monofluoroacetate (6.5 gm., 94%) as a colorless, viscous, very hygroscopic liquid.

*Glyceryl Trismonofluoroacetate*

Fluoroacetyl chloride (29.2 gm., 0.3 mole) was added dropwise to a solution of glycerol (9.2 gm., 0.1 mole) and pyridine (26.4 gm., 0.33 mole) in dry benzene (200 ml.) maintained at  $-10^{\circ}$ . The mixture was allowed to stand at room temperature for two days. It was then washed twice with water, and dried over anhydrous sodium sulphate. The benzene was removed by distillation, and a high boiling fraction of glyceryl trismonofluoroacetate (10.3 gm., 38%) was collected.

*Esters of 2-Fluoroethanol (Compounds 17-28)*

The simple esters are represented by the following example:

*2-Fluoroethyl laurate*.—A mixture of 2-fluoroethanol (7) (75 gm., 1.17 moles), lauric acid (75 gm., 0.375 mole), and sulphuric acid (10 ml.) was heated under reflux for three to four hours. The mixture was cooled and diluted with water. It was then extracted with ether, and the extracts washed successively with water, 10% sodium carbonate, and water again. After the extracts were dried over anhydrous sodium sulphate and the ether was removed, 2-fluoroethyl laurate (78.4 gm., 85%) was obtained as a colorless, pleasant-smelling liquid.

The solid esters were prepared in a similar manner. After removal of the ether, colorless solids were obtained, which were recrystallized several times from ethanol or methanol, the solutions being cooled very slowly with stirring to avoid the formation of oils.

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# DOUBLE ENREGISTREMENT PHOTOÉLECTRIQUE ET MANOMÉTRIQUE DE RÉACTIONS RAPIDES EN PHASE GAZEUSE

## APPLICATION AUX FLAMMES FROIDES<sup>1</sup>

PAR J. R. JUTRAS,<sup>2</sup> E. G. LÉGER<sup>3</sup> ET C. OUELLET

### RÉSUMÉ

On a réalisé un appareil comprenant un oscillographe à double faisceau et à balayage lent et unique, déclenchable manuellement, automatiquement ou avec délai, permettant l'enregistrement simultané de deux caractéristiques d'un phénomène transitoire de durée comprise entre 0.01 sec. et 20 sec. Appliqué à l'étude des flammes froides, cet instrument utilise soit deux photomultiplicateurs, soit un photomultiplicateur et un manomètre sensible et rapide comprenant une membrane et une triode à plaque mobile. Il enregistre les variations de l'émission lumineuse et de la pression et permet de mesurer leur degré de synchronisme ainsi que les périodes d'induction et les vitesses de propagation.

### INTRODUCTION

Les techniques spéciales décrites dans ce mémoire ont été élaborées en vue de l'étude quantitative des pulsations de la faible luminosité et de la pression associées à la propagation d'une flamme froide dans un système statique. Ces techniques sont susceptibles d'applications à d'autres phénomènes transitoires.

L'oxydation en phase gazeuse d'un grand nombre de substances organiques donne lieu, dans un certain domaine de températures et de pressions, à une combustion partielle désignée sous le nom de "flamme froide" (14). Les pulsations de pression liées à ce phénomène ont déjà été enregistrées au moyen d'appareils construits par Aivazov et Neumann (1), Ermakova (4), Fréling et Laffitte (6), Dugleux (3) et autres (8, 15). Celles de l'émission lumineuse ont fait l'objet de bon nombre d'observations visuelles (2, 8, 9), mais leur enregistrement photoélectrique en fonction du temps ne semble avoir été réalisé que par Ouellet, Léger et Ouellet (13) et par Gray (7). Les résultats obtenus par les chercheurs précédents établissent le caractère périodique du phénomène et sont en accord qualitatif avec les schémas réactionnels proposés par Frank-Kamenetskii et Salnikov (5) et par Walsh (16). L'analyse mathématique de la cinétique de réactions autocatalytiques faite par Moore (11) semble expliquer en principe les pulsations observées et leur amortissement.

Une étude plus détaillée de ce phénomène nécessitait la coordination de plusieurs organes capables d'enregistrer les variations de la pression, de la lumière et de la composition du mélange gazeux au cours d'une flamme froide. Il était intéressant de mesurer aussi les vitesses de propagation, qui ne semblent pas avoir été étudiées dans le cas de l'allumage spontané. Ces divers para-

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mètres peuvent maintenant être mesurés simultanément en utilisant conjointement d'une part le spectromètre de masse panoramique pour analyse de gaz en réactions rapides (10) réalisé dans notre laboratoire et, d'autre part, les techniques photoélectrique, manométrique et oscillographique présentées dans ce mémoire avec quelques exemples des résultats qu'elles permettent d'obtenir.

#### DESCRIPTION DE L'APPAREIL

L'appareil comporte un système servant à la préparation des mélanges de carburant et d'oxygène destinées à la production de flammes froides, une chambre à réaction montée de façon à permettre des observations visuelles et des observations par photomultiplicateurs tout en évitant les gradients thermiques, un manomètre sensible et rapide et, enfin, un oscilloscope à double faisceau ayant un balayage lent, unique et de durée réglable, qui peut être déclenché soit dans un délai prédéterminé, soit par le phénomène lui-même. On peut enregistrer simultanément, en photographiant l'écran de l'oscilloscope, deux paramètres de la flamme froide; par exemple, la pression et l'émission de lumière ou bien la lumière provenant de deux parties de la chambre à réaction. En faisant déclencher le balayage par l'admission soudaine des gaz, on obtient une mesure précise du retard à l'inflammation froide. L'écart entre les instants de passage de la pulsation lumineuse en deux sections de la chambre à réaction donne une mesure de la vitesse de propagation. Toutes ces données sont susceptibles de contribuer à l'interprétation du phénomène.

#### *Production et observation des flammes froides*

La flamme froide a lieu dans un cylindre en Pyrex C (Figure 1) de 4.6×21 cm., entouré d'un manchon en laiton E destiné à uniformiser la température. Le tout est contenu dans un four en fer F chauffé électriquement. La tempéra-

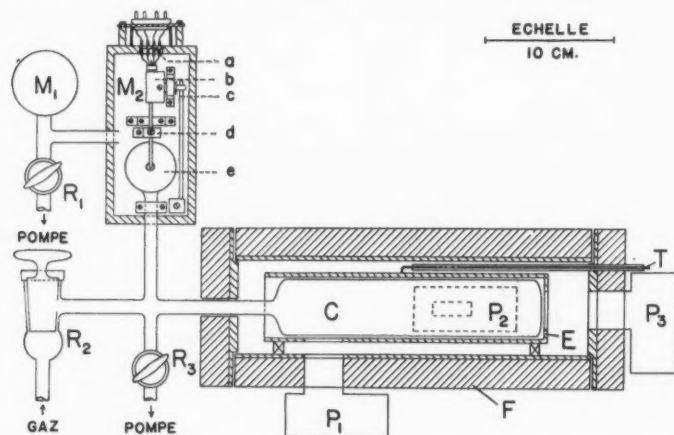


FIG. 1. Chambre à réaction C, monomètre  $M_2$  et emplacements des photomultiplicateurs  $P_1$ ,  $P_2$  et  $P_3$ .



ture, mesurée au moyen de thermocouples T, est uniforme à  $\pm 0.5^\circ\text{C}$ . près. Le système est évacué au moyen d'une pompe Hyvac à travers deux pièges refroidis par un mélange de glace sèche et d'acétone. Le mélange gazeux, préparé quelques heures à l'avance suivant une méthode déjà décrite (13), est introduit soudainement par le robinet creux R<sub>2</sub>. Suivant les renseignements désirés, on enregistre les indications de deux des organes suivants: le manomètre M<sub>2</sub> et les photomultiplicateurs de type 931A, situés dans les positions P<sub>1</sub>, P<sub>2</sub> et P<sub>3</sub>, d'où la lueur est observée de différents points de vue. L'un des côtés du four porte une fente longitudinale d'un centimètre de largeur, recouverte d'une lame de verre, que l'on peut démasquer pour faire des observations visuelles.

Pour éviter leur échauffement par le four, les multiplicateurs sont montés dans des cylindres en laiton munis de fenêtres et refroidis par circulation d'eau dans des serpentins en cuivre. Le robinet R<sub>3</sub> est lubrifié avec de la graisse Apiezon T dont le point de fusion est de  $125^\circ\text{C}$ . Les tubes de verre sont noircis à l'extérieur jusqu'à une distance de 10 cm. du four pour empêcher la lumière de pénétrer dans ce dernier.

#### *Le traducteur de pression*

Dans le manomètre différentiel sensible et rapide représenté en M<sub>2</sub> (Figure 1), la plaque mobile d'une triode RCA 5734 est commandée par le déplacement d'un diaphragme.

Une variation de pression est convertie en déplacement mécanique par la déformation du diaphragme circulaire "e" en alliage cuivre-béryllium, à surface ondulée de 4 cm. de diamètre, provenant d'un manomètre Fisher et protégé contre le contact des gaz par un mince enduit d'Araldite SN985 Ciba déposé sur la face intérieure. Ce diaphragme est collé au moyen d'Araldite 101 sur une capsule en verre à tubulure latérale enfermée dans une chambre étanche en laiton où règne la pression de référence mesurée sur un manomètre M<sub>1</sub> de type Edwards. Le déplacement du centre du diaphragme en fonction de la différence de pression est linéaire à 1% près jusqu'à 190 mm. Hg, où il est de 833 microns.

Le déplacement mécanique linéaire du diaphragme "e" est converti en déplacement angulaire au moyen d'une tige creuse en duralumine L (Figure 2), dont l'extrémité est liée à la plaque mobile P de la triode RCA 5734, la membrane flexible M de cette dernière constituant le point d'appui du levier. Le

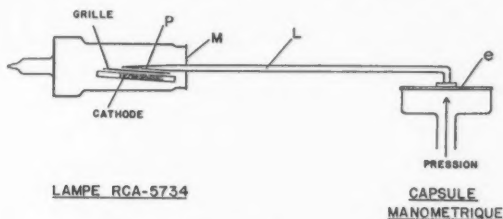


FIG. 2. Schéma illustrant le principe du manomètre.



courant de plaque de cette lampe est fonction de la position de la plaque P et, par suite, de la pression qui règne en "e"; le signal électrique obtenu varie linéairement à 1% près jusqu'à une pression d'au moins 100 mm. Hg où il est de 6.7 V. pour une résistance de charge de 1 mégohm et une tension de plaque de 300 V. La sortie de cette lampe est reliée à l'oscilloscope à travers un premier stage d'amplification.

La lampe 5734 est enchâssée dans une douille en laiton "b" dont la tige latérale pivote dans une bague vissée à la boîte (Figure 1). Cette tige est liée à un levier "c", de sorte que la position angulaire de la lampe est réglée et maintenue par un vis agissant contre un ressort à l'autre extrémité de ce levier. Des butoirs "d" limitent le déplacement angulaire de la plaque de la lampe et le déplacement linéaire de la membrane, de sorte qu'un excès de pression ne fait subir à ce montage aucune déformation permanente.

Le retard à l'enregistrement d'une pulsation de pression doit être, dans notre cas, inférieur au centième de seconde. Olson (12) affirme que la triode 5734 peut suivre des vibrations jusqu'à une fréquence de  $10^4 \text{ sec.}^{-1}$ . Nous avons constaté sur l'oscilloscope que l'ensemble de notre montage répond à des ondes sonores de l'ordre de  $10^3 \text{ sec.}^{-1}$ . Plus à craindre était le retard à la transmission d'une pulsation de pression ayant à parcourir une distance de 20 cm. dans le tube de verre de 5 mm. de diamètre qui relie la chambre à réaction au manomètre. Nous avons cependant vérifié, sur l'oscilloscope, qu'une compression soudaine de 50 mm. Hg franchit en moins de  $10^{-2} \text{ sec.}$  une distance de 1 mètre entre deux capsules manométriques branchées sur un tube de 5 mm. de diamètre. Ceci permet de conclure que nos enregistrements manométrique et photoélectrique sont synchrones à au moins  $10^{-2} \text{ sec.}$  près.

#### *L'oscillographe à double faisceau*

Le diagramme fonctionnel de la figure 3 donne une vue d'ensemble des divers circuits utilisés et permet de voir leur enchaînement. Ces circuits sont reproduits en détail à la figure 4.

Trois sources de tension alimentent les diverses parties de l'appareil: une

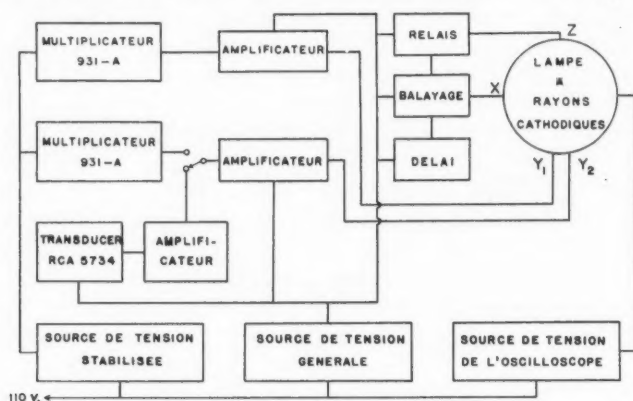


FIG. 3. Bloc-diagramme.

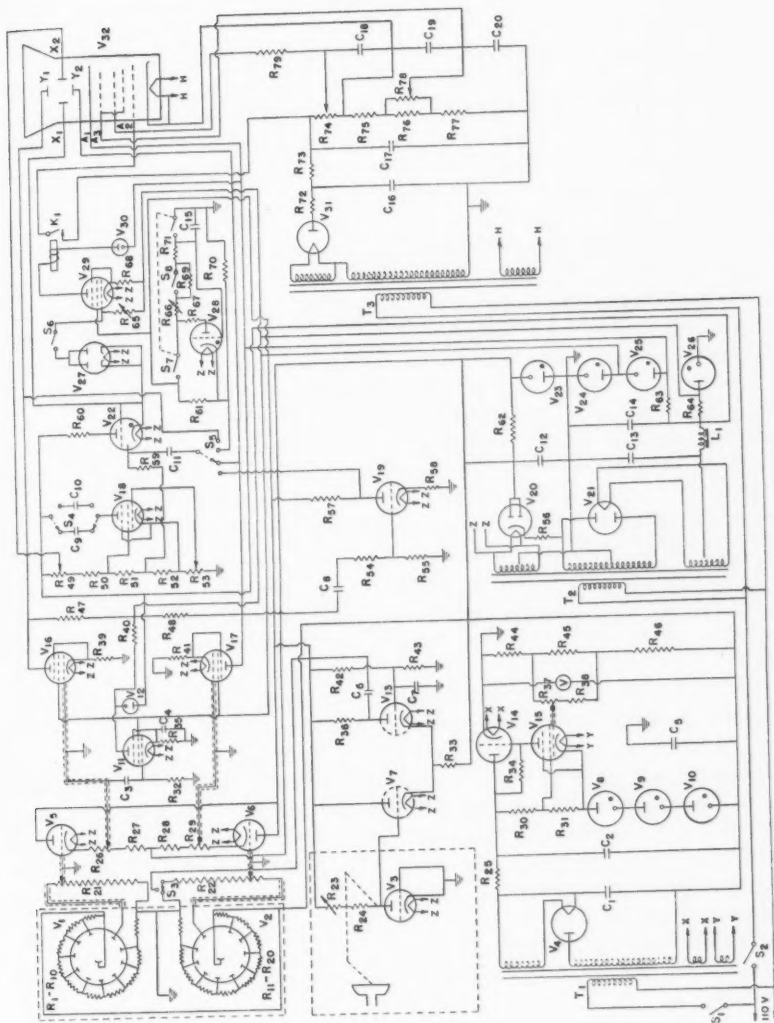


Fig. 4. Circuits électriques.

source de 1000 V. stabilisée à un facteur de 250 pour les photomultiplicateurs; une source de 2000 V. pour la lampe cathodique; une source fournissant les tensions nécessaires aux circuits auxiliaires d'amplification et de balayage ainsi qu'au circuit du manomètre.

Chaque multiplicateur  $V_1$  et  $V_2$  (de type 931A) est maintenu sous une différence de potentiel de 100 V. par plaque. Le courant photoélectrique, multiplié par un facteur de  $10^5$  à  $10^6$ , sort de l'anode et produit, à travers un diviseur ajustable  $R_{21}$  ou  $R_{22}$  (20 mégohms), une chute de potentiel appliquée à l'une des grilles d'une double triode  $V_4$  ou  $V_5$  (6SN7), montée en cathode suiveuse. Le signal résultant est amplifié au moyen d'une pentode  $V_{13}$  ou  $V_{14}$  (6AC7) et appliqué à l'une des plaques  $Y_1$  et  $Y_2$  de déviation verticale de la lampe à rayons cathodiques (de type Cossor 89J à double faisceau). L'intermodulation des faisceaux étant inférieure à 5%, nous ne l'avons pas supprimée.

Le circuit de balayage diffère des circuits ordinaires qui requièrent une amplification subséquente et dont les périodes sont en général beaucoup trop courtes pour l'enregistrement d'une flamme froide. Celle-ci dure en effet environ une seconde. Dans notre circuit, un condensateur  $C_6$  ou  $C_7$  est chargé à travers une pentode 6SJ7 à un taux contrôlé par une résistance variable à plots  $R_{47}$  jusqu'à un potentiel fixe, auquel une diode  $V_{23}$  (6H6) commence à conduire et empêche le potentiel d'atteindre la valeur nécessaire pour déclencher la décharge d'une thyatron  $V_{18}$  (2050). Cette décharge n'a lieu que si la grille de la thyatron reçoit une impulsion positive, signal provenant d'un photomultiplicateur ou du manomètre et annonçant le début du phénomène à enregistrer. Le condensateur ainsi déchargé permet l'amorce d'un nouveau balayage car le circuit oscillant produit par  $C_6$  ou  $C_7$ ,  $V_{18}$ ,  $R_{53}$  et l'inductance des fils éteint  $V_{18}$  après la décharge. Quand  $V_{23}$  conduit le courant qui normalement chargerait  $C_6$  ou  $C_7$ , il se produit une chute de potentiel aux bornes de  $R_{60}$ . Ceci empêche la pentode  $V_{25}$  (6SH7) de conduire et met en action le relais  $K_1$  qui, en abaissant le potentiel de grille de la lampe cathodique, supprime la tache lumineuse sur l'écran.

Un circuit de délai mis en action manuellement peut retarder le déclenchement du balayage jusqu'à un temps maximum de 16 sec. En ouvrant le commutateur  $S_6$ , on charge le condensateur  $C_{12}$  à travers les résistances  $R_{57}$ ,  $R_{58}$  (fixes) et  $R_{55}$  (variable) jusqu'à un potentiel déterminé auquel la lampe à gaz 605 envoie sur la grille de la thyatron une pulsation positive suffisamment forte pour déclencher le balayage.

Pour le fonctionnement du manomètre, un circuit d'amplification est utilisé. On emploie une double triode 6SN7. Le signal amplifié est appliqué au même endroit que celui d'un photomultiplicateur, mais en raison de sa polarité négative, il doit être repris et inversé au moyen d'une triode 6J5 pour le rendre apte à actionner la décharge de la thyatron. Le manomètre peut ainsi déclencher le balayage au moment où le gaz pénètre dans la chambre à réaction, ce qui rend possible la mesure précise de la période d'induction de la flamme froide.

L'enregistrement se fait par voie photographique au moyen d'une camera fixe utilisant des papiers sensibles.

## EXEMPLES DE RÉSULTATS

On voit sur la figure 5 quatre photos d'oscillogrammes, portant chacune une échelle de temps en secondes. Celles de gauche portent en outre une échelle d'intensités lumineuses  $H$  en unités arbitraires et de pressions  $\Delta P$  en mm. Hg.

Dans les oscillogrammes 1411 et 1448, les courbes  $P$  représentent l'évolution de la pression. Après le déclenchement du balayage par l'entrée soudaine des gaz, la pression atteint rapidement une valeur qui reste stable, jusqu'à l'appari-

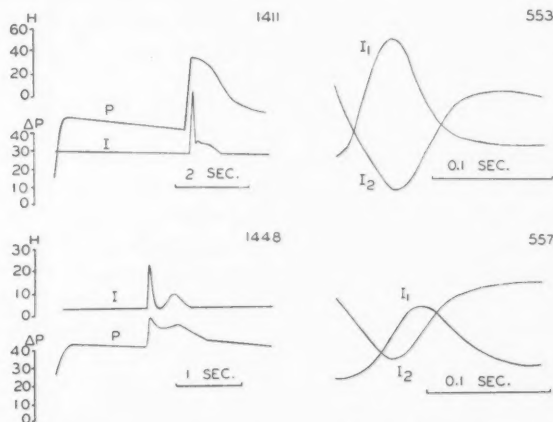


FIG. 5. Oscillogrammes illustrant l'enregistrement simultané de l'intensité lumineuse  $I$  et de la pression  $P$  (à gauche) et des intensités lumineuses perçues par deux photomultiplicateurs en positions différentes (à droite).

tion de la flamme froide marquée par une pulsation subite suivie d'une décroissance et, dans certains cas, d'une ou plusieurs pulsations subséquentes. La pression finale reste supérieure à ce qu'elle était avant la flamme. L'abaissement graduel et linéaire de la trace  $P$  résulte de la décharge d'un condensateur du circuit du manomètre; on tient compte de cet effet en appliquant une correction établie par des mesures faites avec des gaz inertes. La trace  $I$  représente l'intensité de la luminescence vue par un photomultiplicateur en position  $P_3$  de la figure 1. Nulle avant et après la flamme froide; la luminescence atteint rapidement un maximum au moment de l'allumage; ses pulsations suivent de très près celles de la pression. En observant la luminescence de l'une des positions  $P_1$  et  $P_2$ , on observe généralement, entre la courbe de lumière et la courbe de pression, un certain décalage qui semble lié à la vitesse de propagation de la flamme froide.

Les oscillogrammes rapides 553 et 557 de la partie droite de la figure 5 représentent les intensités lumineuses  $I_1$  et  $I_2$  d'une même flamme observées simultanément par deux photomultiplicateurs en positions  $P_1$  et  $P_2$  de la figure 1. Le balayage a été déclenché dans ce cas par le signal provenant de l'un des photomultiplicateurs. En 557, les maxima accusent un décalage d'environ 0.025 sec., temps qu'a mis le phénomène pour se propager sur la

distance de 12 cm. de  $P_2$  à  $P_1$ . On en conclut que la flamme s'est allumée à l'extrémité droite de la chambre à réaction et s'est propagée vers le tube d'entrée des gaz à une vitesse moyenne d'environ 500 cm./sec., sans déformation appréciable si l'on en juge par l'allure semblable des deux courbes. Le synchronisme des courbes 553 semble indiquer à première vue une lueur statique dont l'évolution passe en même temps par les mêmes phases dans toute l'étendue de la chambre à réaction. Cependant, un examen minutieux et la confrontation de cet oscillogramme avec d'autres obtenus à des pressions légèrement différentes montrent qu'il s'agit très probablement d'une flamme qui se propage en sens inverse de la précédente et à une vitesse beaucoup plus grande. Les décalages observés dans la plupart des cas sont plus grands que ceux-ci et correspondent généralement à des vitesses de propagation de l'ordre de 50 cm./sec.

Voici quelques exemples de relations obtenues à partir de séries d'oscillogrammes. La figure 6 montre comment varie la période d'induction de la flamme froide de l'éther butylique en fonction de la température et de la pression. Dans la figure 7, on voit l'influence de la pression initiale d'un mélange gazeux sur les amplitudes de la première et de la deuxième pulsations  $\Delta P_1$  et  $\Delta P_2$ , ainsi que l'accroissement permanent de pression  $\Delta P_F$  provoqué par le passage de la flamme. Quelques résultats concernant les vitesses de propagation de flammes

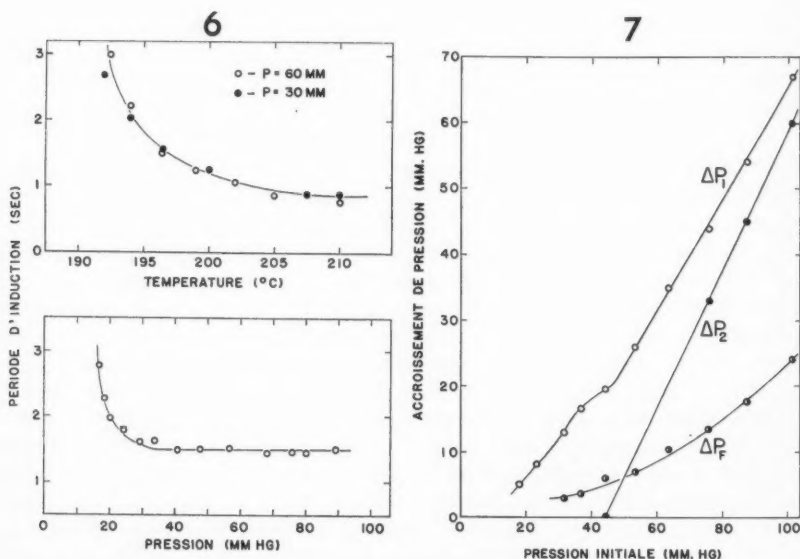


FIG. 6. Influences de la température et de la pression (à 198°C.) sur la période d'induction de la flamme froide de mélanges contenant 5% d'éther dibutylique et 95% d'oxygène.

FIG. 7. Influence de la pression initiale d'un mélange à 70% d'éther diéthylique à 190°C. sur la première et la seconde pulsations de pression  $\Delta P_1$  et  $\Delta P_2$ , ainsi que sur l'accroissement final et permanent  $\Delta P_F$  de la pression après le passage d'une flamme froide.

froides d'éther méthylique sont présentés dans la figure 8. On voit que dans une certaine zone de pressions, la vitesse subit des variations importantes et capricieuses qui vont jusqu'à un changement de signe.

Divers résultats obtenus par cette méthode seront présentés et discutés dans une autre publication.

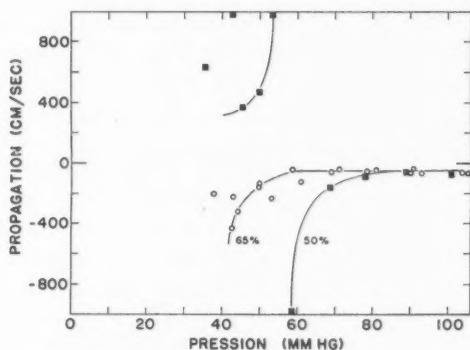


FIG. 8. Vitesse de propagation, à diverses pressions, d'une flamme froide dans des mélanges contenant 50% et 65% d'éther diméthylique, à 253°C.

#### CONCLUSION

L'appareil réalisé permet de mesurer, avec une précision au moins égale au degré de reproductibilité des phénomènes, plusieurs caractéristiques des flammes froides dont la connaissance, jusqu'ici surtout qualitative, est nécessaire à l'interprétation de cette étape de la combustion.

Les techniques mises au point sont susceptibles d'être appliquées à l'étude d'autres phénomènes transitoires de durée comparable à celle des flammes froides.

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#### SUMMARY

An apparatus is described, which records simultaneously two characteristics of a transient phenomenon over time intervals ranging from 0.1 sec. to 20 sec. It comprises a double-beam oscillograph, with a slow, single sweep which can be triggered either manually, automatically, or by delayed action. In a study of cool flames, this instrument is used in connection with either two photomultipliers or one photomultiplier and a manometer. In this rapid, sensitive manometer, the gas-loaded diaphragm acts upon the movable plate of a triode. Light and pressure pulses are followed in detail and it is possible to study their degree of synchronization, as well as the induction periods and propagation velocities of cool flames.

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## NOTES

THE EFFECT OF TEMPERATURE AND ACIDITY ON THE DRY STORAGE OF SODIUM CARRAGEENATE<sup>1</sup>

BY D. A. I. GORING

Carrageenin is the hydrocolloid extractable with water from the red seaweed, Irish moss. In recent work there was evidence that the dried extract, on storage, degraded and gave solutions of decreased viscosity (1, 4). Since viscosity is an important practical and fundamental property of the polysaccharide, further experiments were done to find the best conditions for storage.

Extractions were made at 60°C. on the residue of an extraction at 30°C. This method would be expected to yield mostly the gelling component (2).

Solutions of the extract were dialyzed for 24 hr. with internal stirring against 0.02 *M* sodium acetate to exchange all the cations for sodium. The acetate was removed by dialysis against distilled water. The hydrocolloid was then obtained as a white, spongy solid by freeze-drying. The water contents of the freeze-dried samples were between 5 and 10%. During the final stage of dialysis the "acidity" of the product could be controlled. Prolonged dialysis caused a marked lowering of pH owing to the removal of sodium ions and the formation of carrageenic acid. Dialysis against a low concentration of NaOH (e.g., 100 mgm./liter) resulted in a solution of pH 8-10. The pH of a 0.3% solution in distilled water was taken as an empirical measure of the acidity of a sample.

The degradation was followed by the change in viscosity of freshly prepared solutions in an acetate buffer (pH = 5.5; *I* = 0.05). The specific viscosity,  $\eta_{sp}$ , was measured in modified Ubbelohde viscometers as previously described (1). The intrinsic viscosity,  $[\eta]$ , was determined from

$$[\eta] = (\eta_{sp}/c)_{c \rightarrow 0}$$

where *c* is the concentration of the solute. The value of  $(\eta_{sp}/c)_{c=0.1\%}$  was also recorded as a practical estimate of the viscosity at a working concentration of 0.1%.

Samples were stored in screw-cap bottles at room temperature (ca. 25°C.), 4°C., and -13°C. To eliminate condensation care was taken to bring the cold-stored samples to room temperature before opening.

Three samples were studied in detail. Samples 1, 2-A, and 2-B had acidities of 5.0, 6.9, and 9.5 respectively. Samples 2-A and 2-B were part of the same extraction in which the acidity was controlled by addition of NaOH to the distilled water for dialysis. With Sample 1, extracted from another batch of seaweed, the pH decreased on prolonged dialysis to give an acidity of 5.0. Variation of  $[\eta]$  and  $(\eta_{sp}/c)_{c=0.1\%}$  with days of storage at various temperatures is shown in Tables I and II. An empirical measure of the rate of degradation was the ratio of the initial value of  $(\eta_{sp}/c)_{c=0.1\%}$  to the value after 60 days' storage (Table III).

<sup>1</sup>Issued as N.R.C. No. 3766.

TABLE I  
DECREASE OF VISCOSITY ON STORAGE FOR SAMPLE 1

Temperature	Days stored	$[\eta]$ gm. <sup>-1</sup> dl.	$(\eta_{sp}/c)_{c=0.1\%}$
Room	0	13.8	21.6
"	21	5.3	5.8
"	59	4.0	4.3
4°C.	0	13.8	21.6
"	21	11.6	15.4
"	59	9.1	11.8
"	142	5.8*	6.2*

\*These measurements were made at an ionic strength of 0.13. A relatively small factor was applied to correct to an ionic strength of 0.05.

TABLE II  
DECREASE OF VISCOSITY ON STORAGE FOR SAMPLES 2-A AND 2-B

Temperature	Days stored	$[\eta]$ gm. <sup>-1</sup> dl.		$(\eta_{sp}/c)_{c=0.1\%}$	
		2-A	2-B	2-A	2-B
Room	0	24.9	23.9	61.5	48.3
"	87	20.7	20.4	40.9	40.1
"	295	14.7	18.0	26.7	31.0
"	541	12.0	15.7	19.2	27.7
4°C.	0	24.9	23.9	61.5	48.3
"	90	23.7	21.4	51.5	44.1
"	295	22.6	21.6	48.3	42.3
"	544	21.6	21.3	47.0	43.7
-13°C.	0	24.9	23.9	61.5	48.3
"	91	23.8	21.9	51.9	47.7
"	300	22.7	22.0	47.0	45.0
"	545	23.2	21.3	49.7	43.7

TABLE III  
RATIO OF INITIAL VALUE OF  $(\eta_{sp}/c)_{c=0.1\%}$  TO VALUE  
AFTER 60 DAYS' STORAGE

Temperature of storage	Sample	Acidity, pH	Ratio
Room	1	5.0	5.02
"	2-A	6.9	1.30
"	2-B	9.5	1.13
4°C.	1	5.0	1.85
"	2-A	6.9	1.12
"	2-B	9.5	1.06
-13°C.	2-A	6.9	1.11
"	2-B	9.5	1.01

Some further measurements were attempted on samples which were dialyzed to a pH of 3. Marked degradation occurred during dialysis leading, in some cases, to a 40-fold decrease in viscosity. On storage at room temperature this material was transformed into a hard black solid.

The data show that an increase in the temperature of storage of a sample accelerates the rate of degradation. This is supported by the known tendency of carrageenin in solution to degrade on heating (3, 5). However, in sample 2-B, the polysaccharide is essentially stable at lower temperatures and there is little difference in the small change in viscosity at 4°C. and -13°C.

The viscosity on storage is also sensitive to the acidity of the sample. Extracts giving solutions of low pH are more unstable. This is further illustrated by the charring of samples with acidity of 3 when stored at room temperature. These results must arise from a marked instability of carrageenic acid. Removal of the sodium ion to give a partially acidic polysaccharide would then produce a tendency for degradation. However if the solid extract is prepared from a solution of pH 9-10, it may be stored at temperatures below 4°C. for long periods without appreciable change in its viscosity.

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#### NOTE ON A CONVENIENT RECORDING TECHNIQUE FOR RAPID CHANGES

BY A. D. MISENER AND C. CROWE

The study of transient heat-flow phenomena requires an examination of the early part of a very rapid temperature rise. The significant part of the temperature vs. time curve is completed in a second or so (Fig. 1) and cannot be recorded satisfactorily with the highest chart-speeds available on conventional electronic recorders (approximately 2 in./min.). A convenient method for recording such rapid changes was developed by combining the output of a conventional recorder with oscilloscope display and photographic recording.

In this method, the 120-cycle output of the recorder amplifier was applied to the vertical deflection plates of an oscilloscope. The sweep period was adjusted to cover the interval of time during which the temperature was to be

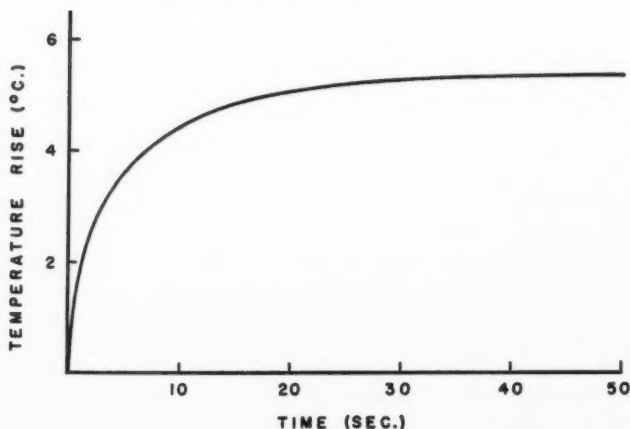


FIG. 1. Typical record of a rapid temperature change on a conventional recorder.

observed, using an external capacitance if necessary. With a sweep period sufficiently large compared to the amplifier period, the trace appeared as a vertical line travelling across the face of the tube with a period equal to the sweep period and an amplitude proportional to the peak to peak voltage of the amplifier output. To calibrate the traverse with respect to time and to provide a record which could be easily corrected for the non-linearity of the sweep, the intensity of the oscilloscope beam was pulsed with a multivibrator. The trace was photographed with a polaroid oscilloscope camera. Typical records are shown in Fig. 2. The vertical position of the trace was adjusted to display the positive half only, permitting greater amplification of the voltage rise.

The particular application of this technique to the measurement of a rapid temperature rise required the starting of the record at the time a switch was closed to energize a heater. This was accomplished by setting the oscilloscope on driven sweep and adjusting the sweep triggering amplitude above the steady state amplifier output. The closing of the heater switch discharged a capacitor through the vertical deflection input, triggering the sweep. The discharge time of the capacitor was short enough to have negligible effect on the amplifier trace. The triggering amplitude could be adjusted to permit the recording of one or more traverses on the same film. Successive traverses provide a continuation of the record with increasing amplitude up to the limit of the tube face.

In Fig. 2 the nearly horizontal trace (i.e., constant temperature) was obtained before energizing the heater and served as a base line from which to calculate the temperature vs. time curve. A simple calibration will convert the height of the lines from the base line into actual temperature readings if these are needed. A block diagram of the circuit used in this particular application of the method is shown in Fig. 3.

PLATE I

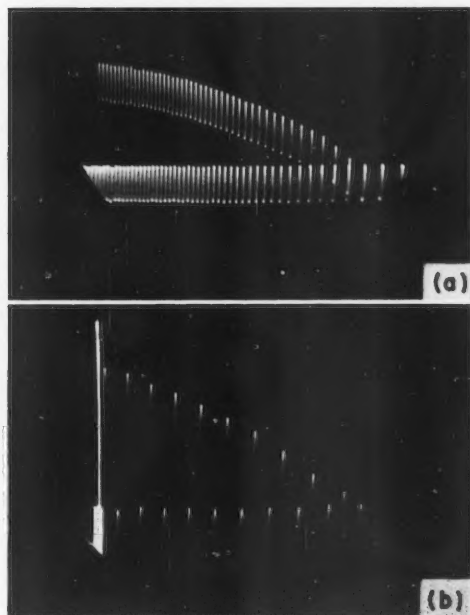


FIG. 2. Records with oscilloscope and camera (time increasing right to left).  
 (a) sweep period approximately 2 sec., 1/30 sec. intervals.  
 (b) sweep period approximately 1/6 sec., 1/60 sec. intervals.



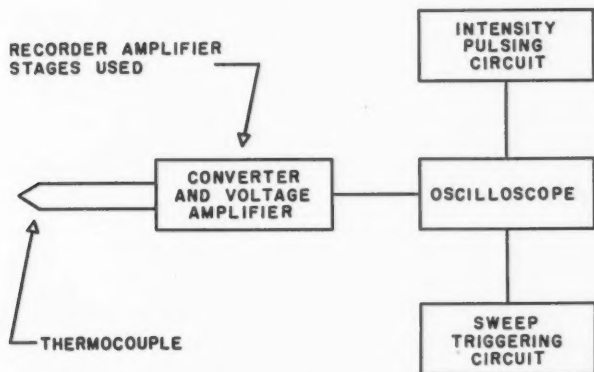


FIG. 3. Block diagram of the circuit used.

We wish to express appreciation for a grant from the Division of Building Research, National Research Council, which supports the research on heat flow phenomena, during which this method was developed. One of us (C. C.) also gratefully acknowledges assistance in the form of a National Research Council Scholarship.

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